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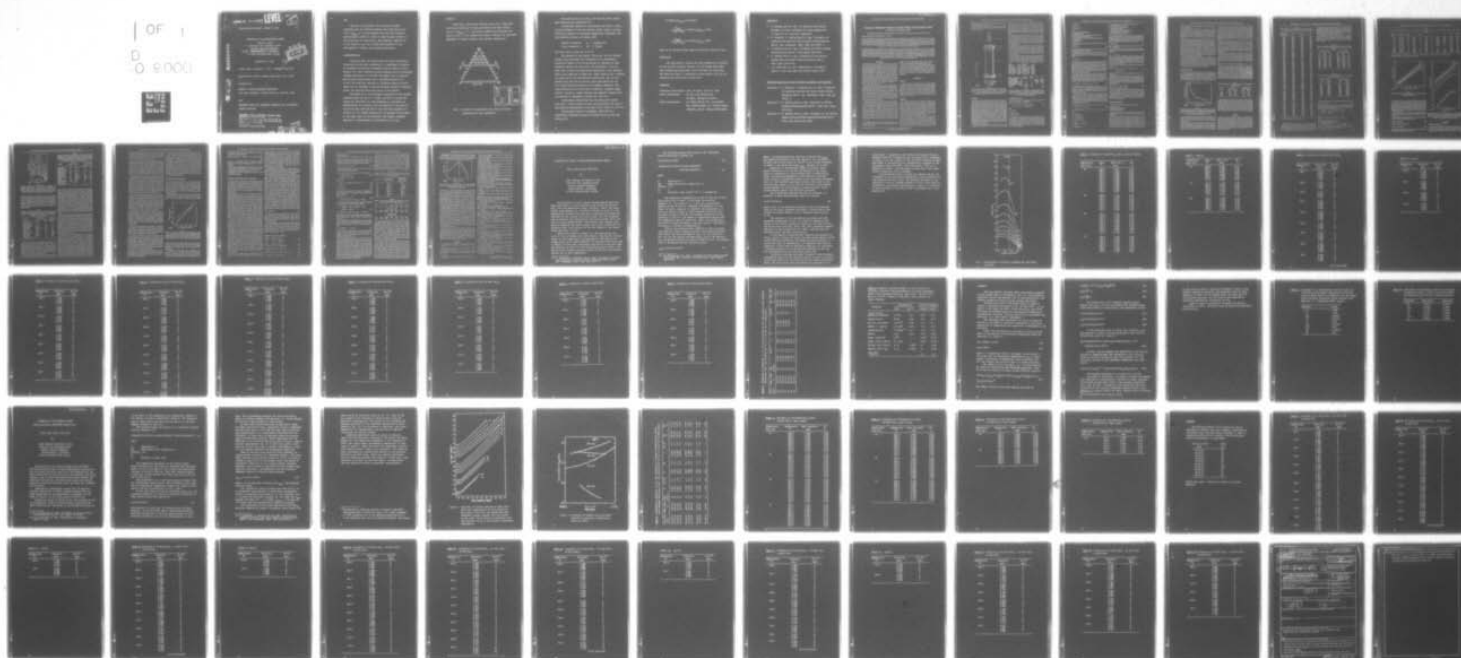
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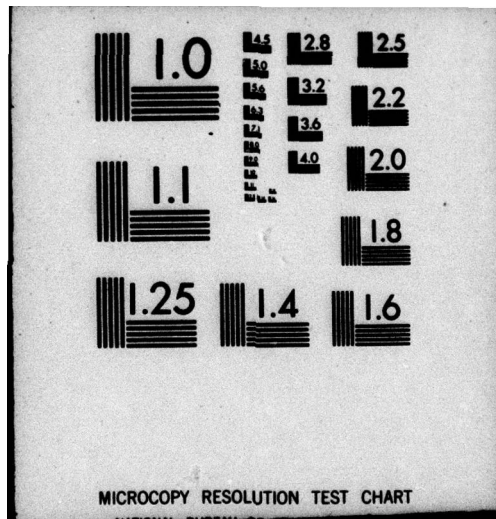
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VISCOSITY OF CHLOROALUMINATE MELTS

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AIM

The aim of the project was to obtain reliable viscosity data for mixtures between LiCl-NaCl-AlCl_3 with $0.50 \leq x_{\text{AlCl}_3} \leq 1.00$ and combine the data with previous spectroscopic studies in order to gain further insight of the structures of these melts. The technical implication of the study is the use of these melt mixtures in the development of thermal and secondary batteries.

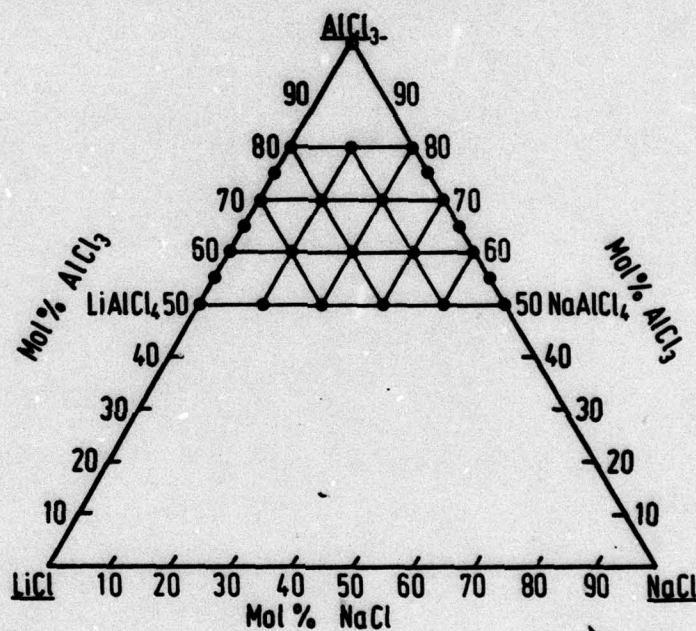
INSTRUMENTATION

Viscosity data for molten salts has been notoriously unreliable and we have considered it a challenge to develop an automated oscillation viscometer with no need for calibration [1]. This viscometer gives viscosity with an estimated standard deviation of 0.2% when the utmost care is applied. More routine measurements give a standard deviation of 0.5-1%. Our work has resulted in viscosity values for NaCl which will be accepted as the new National Bureau of Standard value. The previous NBS value was up to 50% higher.

The adaption of the developed techniques to the present studies needed the use of a closed container in which the liquid was contained [2]. The mathematical solutions for determination of viscosity from the damping of the oscillations have been obtained and it has also been possible to correct for the formed meniscus due to wetting of the liquid in the upper part of the container. The overall standard deviation in measurements is estimated to 0.5-0.6%.

RESULTS

Pure AlCl_3 , the binary mixtures AlCl_3 - LiCl , AlCl_3 - NaCl and ternary mixtures of AlCl_3 - LiCl - NaCl have been studied for $0.5 \leq x_{\text{AlCl}_3} \leq 1$. The actual compositions measured are given in Fig. 1. The temperature range is between 100 and 300°C dependent on vapour pressure and liquidus temperature.



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Fig. 1. Diagram of compositions for which viscosity determinations were performed.

The results for pure AlCl_3 and the AlCl_3 -NaCl system have recently been published [2].

It has been possible to rationalize the data in terms of the existence of the melt species AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$ and Al_2Cl_6 assuming an Arrhenius temperature dependence and the Arrhenius mixing rule being valid:

$$\text{Species viscosity: } \eta_1 = A_1 \exp(B_1/T)$$

$$\text{Total viscosity, } \eta: \ln \eta = \sum X_i \ln \eta_i$$

The model gave a total fit of 0.4%.

The results of the system AlCl_3 -LiCl and the ternary system AlCl_3 -LiCl-NaCl are presented as two preliminary scientific reports [3,4]. As we wanted to complete all measurements before the AlCl_3 -LiCl was published it has not been time to make the publication manuscripts (last measurements were completed 14 days ago). These results will, however, be submitted as two publications within 1979, one for the system AlCl_3 -LiCl by us and one joint publication by the F.J. Seiler Lab. and Institute of Inorganic Chemistry. The last publication will give data on density, liquidus temperature, viscosity, vapour pressure and specific conductivity as outlined in agreement of March 9th, 1978 [5].

Provisional calculations for the AlCl_3 -LiCl system show that a similar model as that for AlCl_3 -NaCl will give a satisfactory description of the data with a total fit of 0.3%.

The ternary system is attempted described as a quasibinary Arrhenius mixture of the binaries AlCl_3 -NaCl and AlCl_3 -LiCl:

$$\ln \eta(\text{AlCl}_3(\text{X}_{\text{AlCl}_3}), \text{LiCl}, \text{NaCl})$$

$$= \frac{\text{X}_{\text{LiCl}}}{\text{X}_{\text{LiCl}} + \text{X}_{\text{NaCl}}} \ln \eta(\text{AlCl}_3(\text{X}_{\text{AlCl}_3}) - \text{LiCl})$$

$$+ \frac{\text{X}_{\text{NaCl}}}{\text{X}_{\text{LiCl}} + \text{X}_{\text{NaCl}}} \ln \eta(\text{AlCl}_3(\text{X}_{\text{AlCl}_3}) - \text{NaCl})$$

Some of the mixtures show negative deviation from this rule.

CONCLUSION

The experimental program has been completed as outlined in the original program. Results for the system AlCl_3 -NaCl have already been published, while the data for AlCl_3 -LiCl and AlCl_3 -LiCl-NaCl is presented as data reports and will be submitted for publication within 1979.

PERSONELL

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Junior Researchers: Mr. Helge Rørvik, Mr. Jan Havdahl,
Mrs. Esther Urdahl, Mr. Henning Meyer
Johansen, and Mr. Tharald Tharaldsen.

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1. K. Tørklep and H.A. Øye: "An Absolute Oscillating Cylinder (or Cup) Viscometer for High Temperature". J. Phys. E: Sci. Instrum., submitted.
2. W. Brockner, K. Tørklep and H.A. Øye: "Viscosity of Aluminium Chloride and Acidic Sodium Chloroaluminate Melts", Ber. Bunsenges. Phys. Chem. 83 (1979) 1.
3. K. Tørklep and H.A. Øye: "Viscosity of Acidic Lithium Chloroaluminate Melts". Data report 28/2-1979.
4. K. Tørklep and H.A. Øye: "Viscosity of the Ternary System AlCl_3 - LiCl - NaCl Containing Excess AlCl_3 ". Data report 28/2-1979.
5. L.A. King and H.A. Øye: "Memorandum of agreement", March 9, 1978 (Enclosed with yearly report 1978).

Enclosed Scientific Papers directly related to the project

Enclosure 1: W. Brockner, K. Tørklep and H.A. Øye: "Viscosity of Aluminium Chloride and Acidic Sodium Chloroaluminate Melts". Ber. Bunsenges. Phys. Chem. 83 (1979) 1.

Enclosure 2: K. Tørklep and H.A. Øye: "Viscosity of Acidic Lithium Chloroaluminate Melts". Final data report 28/2-1979.

Enclosure 3: K. Tørklep and H.A. Øye: "Viscosity of the Ternary System AlCl_3 - LiCl - NaCl Containing Excess AlCl_3 ". Final data report 20/2-1979.

Viscosity of Aluminium Chloride and Acidic Sodium Chloroaluminate Melts

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Apparate und Methoden / Salzschnmelzen / Viskosität

The viscosity of NaCl–AlCl₃ melt mixtures has been determined in the range $0.50 \leq X_{\text{AlCl}_3} \leq 0.80$, 160°C to 300°C. The viscosity of pure AlCl₃ was measured over the temperature span 196°C to 286°C. A recently designed oscillating vessel viscometer was used. The method, which utilizes closed cylindrical cups subjected to vapour pressures exceeding 11 atm, is absolute and requires no calibration against reference liquids. Results are corrected for surface effects and for evaporation within the crucible. Applying Arrhenius temperature dependencies and the Arrhenius mixing rule, the viscosity is expressed as a function of temperature and composition with an overall standard deviation of 0.4% when the presence of AlCl₄⁻, Al₂Cl₇⁻, Al₃Cl₁₀⁻, and Al₂Cl₆ is assumed.

Die Viskosität von NaCl–AlCl₃-Schmelzen wurde im Bereich von 50–80 mol-% AlCl₃ und bei Temperaturen von 160–300°C bestimmt. Auch die Viskosität von reinem AlCl₃ wurde im Temperaturbereich von 196–286°C gemessen. Verwendet wurde ein neu entwickeltes Oszillationsviskosimeter. Die Methode, bei der ein druckfester, zylindrischer Behälter eingesetzt wurde, ist eine absolute, und erfordert keinerlei Eichung gegen Bezugs-Flüssigkeiten. Die Ergebnisse wurden aufgrund von Oberflächeneffekten und der Verdampfung im Tiegel korrigiert. Unter Zugrundelegung einer Arrhenius-Temperaturabhängigkeit und der Arrhenius-Mischungsregel läßt sich die Viskosität als Funktion der Temperatur und der Zusammensetzung mit einer Gesamtstandardabweichung von 0,4% wiedergeben, wobei die Anwesenheit von AlCl₄⁻, Al₂Cl₇⁻, Al₃Cl₁₀⁻ und Al₂Cl₆ angenommen wird.

Introduction

The AlkCl–AlCl₃ melts with excess AlCl₃ form a unique class of melts with high acidity, low melting temperatures and bond properties intermediate between covalent and ionic. These properties make them attractive for organic synthesis, electrochemical reaction studies, preparation of subvalent and unusual co-ordination compounds. Boston [1] has given a review of work up to 1969. The low melting temperatures combined with high ionic conductivity point to possible use as electrolytes for thermal batteries [2]. Mixtures of AlkCl and AlCl₃ have also attracted interest in connection with the recent Alcoa process for technical electrolysis in NaCl–LiCl–AlCl₃ melts [3, 4].

The present work is part of a general study of physico-chemical properties of complex-forming liquids. Alkali chloroaluminate melts with excess AlCl₃ ($X_{\text{AlCl}_3} > 0.5$) have been structurally well characterized by Raman spectroscopy [5–8]. Thermodynamic activities have been determined by vapour pressure measurements [1, 9–11] and electrochemical studies [12–21]. These liquids may therefore constitute a touchstone for the use of viscous flow as a probe, or diagnostic tool, in formulating structural models.

Previous investigations in this laboratory [22] of MgCl₂-containing melts showed that the appearance of complexes is not necessarily accompanied by an increase in the viscosity: formation of MgCl₄²⁻ complexes may lead to decreased as well as increased viscosities, demonstrating the long-recognized importance of the role of intermolecular forces in determining viscous flow. In the present system, it is known that the covalent, dimeric Al₂Cl₆ melt has a much lower viscosity [23, 24] than the more ionic NaAlCl₄ [25] despite the higher molecular weight of Al₂Cl₆, an observation also

related to the extraordinarily large excess volume of Al₂Cl₆ (l) [26] through the Batschinskii relation [27].

Finally, it was considered an experimental challenge to use the recently developed third generation viscometer [28] for precision work on these highly hygroscopic and volatile melts. In the present study the accuracy was sufficient to propose a model for the variation of viscosity with composition and temperature.

Experimental

Chemicals

Sodium chloride (p. a., Merck) was dried under vacuum at 400°C for 4 hours in a special crystallization furnace, and then heated above the melting point in N₂. The salt was crystallized from the melt using a cooling rate of 5°C/h. Clear crystals were selected for preparing the NaCl–AlCl₃ mixtures. The aluminium chloride (Fluka, puriss, Eisenfrei) was purified by distillation in vacuo through a quartz filter at approximately 200°C. All handling of the samples was carried out in a drybox under nitrogen with water content less than 3–4 ppm.

Apparatus

The oscillation viscometer used is described in detail elsewhere [28]. For highly volatile liquids, a pressure-tight cylindrical cup (autoclave) containing the sample is connected to the pendulum which is excited in torsional oscillations. The oscillations are followed by means of two fixed photodiodes placed in the path of a laser beam reflected from a mirror on the pendulum. Viscosities are computed on-line, using a PDP 11/10 minicomputer, from logarithmic decrements obtained from recorded time intervals. The viscosity may also be calculated simultaneously, although with less accuracy, from the ratio period(gas)/period(liquid).

The cup (25 mm i. d., 110 mm internal length), made of pure nickel, is shown in Fig. 1. Two cups were used in the present work. The sodium chloroaluminate melts were all measured with a cup having a hemispherical bottom for mathematical convenience (hereafter called the spherecup). This was later replaced with a plane-bottomed cup (hereafter called the flatcup) when the mathematical solution for this type of vessel became available to us. Pure

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AlCl_3 was measured with both types of cups. The cups were pressure-tested by heating with water to 190°C.

The internal diameter of the cup was determined with an accuracy of 1 μm at the Division of Product Engineering and Machine Tools of this university [28].

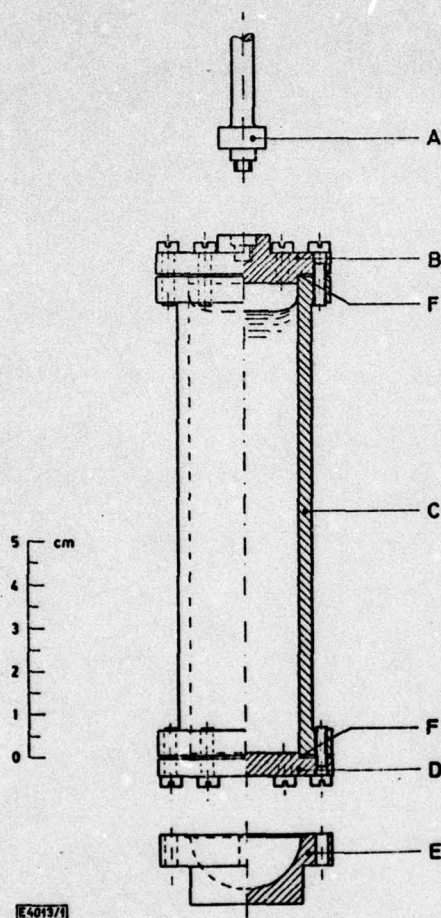


Fig. 1

Nickel cup (autoclave). Four of the six lid/bottom screws are shown. A: Lower part of torsion pendulum (single unit stainless steel). B: Lid. C: Main cylindrical segment. D: Plane bottom ("flatcup"). E: Semispherical bottom ("spherecup"). F: Gold ring seals

Procedure

Calculated amounts of NaCl and AlCl_3 were transferred to a quartz tube with a sealed-in quartz filter. The cell was evacuated on a vacuum-line, sealed and the sample heated to ca. 200°C in a quartz furnace. At this temperature pure AlCl_3 distilled through the quartz filter and condensed in the upper, colder compartment which was kept at room temperature (for reasons of safety). The temperature was then raised to about 500°C, and the approximately 50 mol-% sample remaining in the hot part digested at this temperature over night for removal of impurities. The whole cell, including the distilled AlCl_3 , was subsequently brought to 200°C and the AlCl_3 allowed to flow back through the filter to the main sample. After homogenization by careful shaking, the sample was finally filtered through the quartz filter, leaving the solid impurities in the original chamber. Quartz tubes with internal diameters slightly smaller than that of the nickel cup were used to facilitate introduction of the sample as a single piece.

The viscosity measurements were carried out in N_2 after evacuation of the viscometer to $\sim 10^{-4}$ Torr. Preliminary results

obtained in vacuum did not deviate significantly from viscosities measured in N_2 at atmospheric pressures, and further vacuum runs were discontinued due to the very long thermal equilibration times needed. The period and damping in N_2 with a N_2 -filled cup were determined as functions of the temperature repeatedly during the measuring program. The damping of the N_2 gas inside the cup later displaced by the melt was calculated and corrected for as described below.

The temperature was measured at three points using Pt/Pt10Rh thermocouples connected to a DC differential voltmeter (Model 885 AB, John Fluke Mfg. Co., Inc.). Final reliance was placed on temperature readings taken with the lower thermocouple in contact with the crucible. The measuring thermocouples were calibrated against the melting points of superpure Sn and Ag in special calibration furnaces.

A temperature gradient of about 1°C (upper part hottest) over the furnace zone to be occupied by the Ni-crucible was deliberately introduced to avoid convection currents in the melt. Not less than 2.5–3 hours were allowed for thermal equilibration. About six measurements were carried out at each temperature. Temperature changes were less than 0.1°C in the time required for such a series (ca. thirty minutes).

The measuring procedure was otherwise similar to that described by Törklep et al. [28]. The cup was inspected visually upon removal from the furnace, and weighed if leakage losses were suspected.

A printout example is given in Fig. 2, showing the result of a run in NaCl – 80 mol-% AlCl_3 , nominal composition, at 262.3°C.

SYSTEM	5	RUN NUMBER	25
DATE	280976	PERIODS INCL.	5 - 28
TEMPERATURE, C	262.30	1000/K	1.5676
RADIUS CM	1.25389	PERIOD 25C, MS	2261.50
INERTIA (EXP.)	1274.92	PER. EMPTY, MS	2268.61
INERTIA (PER.)	1274.95	SAMPLE DENSITY	1.46185
SAMPLE WEIGHT	60.4957	LIG. HEIGHT, CM	7.548
DAMPING EMPTY	0.000503	P VAPOUR, TORR	6611.2
P TORR, CORR.	6555.0	% AlCl_3 , CORR.	79.72
DENSITY, CORR.	1.46422	LIG. CM, CORR.	7.398
DISPL. CORR.	0.000036	GAS CH. CORR.	2.512
VAP. DENSITY	0.07617	VAP. VISC., CP	0.0131

PERIOD T (OSC. ZERO)	MS	MEAN	ST-DEV	LEFT	RIGHT
PERIOD (OSC. PEAK)	MS	2274.299	0.013		
OSCILLATION ZERO	MS	2274.298	0.016		
MEAN AMPLITUDES	MM			-0.3679	0.3699
AMPLITUDE DECREASE	MM			239.074	231.602
DAMPING CONSTANT D=10000		133.39	0.07	79.963	71.429
STANDARD DEVIATION *10000				133.47	133.31
VAPOUR DAMPING D=10000		1.07		0.09	0.11
NET DAMPING LIG. D=10000		127.64	0.07		
VISCOSITY	CP	1.1923	0.0015		
LOS CP		0.0764			

Fig. 2

Printout example from runs at 262.3°C in NaCl -80 mol-% AlCl_3 , (nominal composition). The spherecup has been used (see footnote a)); flatcup printouts also contain the viscosity η calculated from the ratio period(gas)/period(liquid)

Calculation of Viscosity

For the spherecup, the following equation was derived for calculation of absolute viscosities [29]

$$2Cx^4 - 2(C + y + 2/3)x^3 + (C + 5y + 4)x^2 - (4 + 35y/8)x + (2 + 1005y/512) = 0 \quad (1)$$

where

$$\mu = 1/(C_1 x^2)$$

$$C = C_2/C_1$$

$$C_1 = (\pi R^3 T)/(\delta I)^*$$

* During the experimental work with the spherecup, an expression for C_1 was used in which T was replaced with the period of oscillation for an empty cup. This unnecessary approximation, introduced at an early stage, is not entirely valid when using our more accurate third generation viscometer. It has been found that the substitution leads to an error of +0.5% in the present NaCl – AlCl_3 viscosities.

$$C_2 = T/(\rho \pi R^2)$$

$$x = b_1 R$$

$$b_1 = ((\pi \rho)/(\eta T))^{\frac{1}{2}}$$

$$y = h/R$$

h : Height of liquid (cylindrical part)

R : Cup internal radius

δ : Logarithmic decrement (damping constant); net value.

T : Period with liquid-containing cup

I : Total moment of inertia of oscillating mechanical system

ρ : Liquid density

η : Liquid viscosity.

Equation (1) is solved for x by usual numerical methods, and η is then given by

$$\eta = 1/(C_2 x^2). \quad (2)$$

The error introduced by Equation (1) is less than 0.1% under present experimental conditions [29].

The moment of inertia with empty cup was measured at 25°C as described in Ref. [28]. The increased momentum of the oscillating system at higher temperatures was calculated from the period increase,

$$I = I^{25}(T_0/T_0^{25})^2 \quad (3)$$

where I and T_0 are the moment of inertia and the period, respectively, with empty cup at the experimental liquid temperature, and T_0^{25} the period at 25°C. The period T_0 was calculated from a temperature function determined in separate experiments (cf. above). The terms INERTIA (PER.) and INERTIA (EXP.) in the printout headings (Fig. 2) refer to moments of inertia corrected by using Equations (3) and (4), respectively. The INERTIA (PER.) value was always used for calculation of viscosities.

The radius of the cup has been corrected using mean thermal expansion coefficients obtained from the literature, from dilatometric measurements and from the period increase with temperature as described in Ref. [28]. The difference is small in terms of calculated viscosities, and the following function obtained from data in Gmelin [30] fits as well as any other for the oscillating cup method:

$$\alpha_{20} = 12.08 \cdot 10^{-6} + 9.75 \cdot 10^{-9} t - 5.54 \cdot 10^{-12} t^2. \quad (4)$$

Liquid densities were calculated from the expressions given by Fannin et al. [31] for the single liquid-phase region. For pure AlCl_3 , the expression of King and Seegmiller [32] was used. These densities were also used to calculate the height of the liquid in the cylindrical part of the cup.

The damping constants measured with the liquid-containing spherecup were corrected for gas damping, gas displacement and vapour damping to give the net values required by Equation (1). The procedure was analogous to that described below for the flatcup.

The following absolute working equations for flatcups (plane bottom and lid) were derived [29] from the general solution given by Beckwith and Newell [33]

$$(\pi \rho h R^4 / (k I)) [A(\Delta p + q)x^{-1} - B \Delta x^{-2} - C p x^{-3} - D x^{-4}] = 1/\omega^2 - 1 + (\Delta - \Delta_0/\omega)^2 \quad (5)$$

$$(\pi \rho h R^4 / (k I)) [A(p - \Delta q)x^{-1} - B x^{-2} + C q x^{-3}] = 2(\Delta - \Delta_0/\omega) \quad (6)$$

where

$$A = 4 + (R/h)$$

$$B = 6 + (16/\pi)(R/h)$$

$$C = (3/2) + 9(R/h)$$

$$D = (3/2) - (8/\pi)(R/h)$$

$$\omega = T_0/T$$

$$p = 1/(2(\Delta + (1 + \Delta^2)^{\frac{1}{2}}))^{\frac{1}{2}}$$

$$q = 1/(2p)$$

$$x = R(2\pi\rho/(\eta T))^{\frac{1}{2}}$$

Δ : Total damping observed with liquid in cup ($\delta/2\pi$)

Δ_0 : Damping correction term ($\delta_0/2\pi$)

$k = \begin{cases} 1 & \text{for the completely filled cup} \\ 2 & \text{for the partly filled cup} \end{cases}$

$h = \begin{cases} \text{half height of cup when completely filled} \\ \text{liquid height when partly filled} \end{cases}$

T_0 : Period of oscillation with empty cup.

The damping coefficients Δ and Δ_0 above are logarithmic decrements δ in units of 2π . The other symbols were defined earlier.

Equations (5) and (6) are used to calculate the viscosity from the period ratio ω and the damping constant, respectively. The equations are solved numerically for x . The viscosity is then given by

$$\eta = 2\pi\rho R^2/(Tx^2). \quad (7)$$

The error in the flatcup solutions is less than 0.1% when $R/h < 1$ and $x > 10$ [29, 34].

All corrections to the measured damping in liquid are contained in the term Δ_0 . Three terms are included in this correction (all in units of 2π)

$$\Delta_0 = \Delta_1 - \Delta_2 + \Delta_3 \quad (8)$$

where Δ_1 is the observed damping constant with empty (gas-filled) cup, Δ_2 is the calculated gas damping of the volume later displaced by the liquid (the displacement correction DISP. CO²R. in Fig. 2), and Δ_3 the calculated damping of the liquid vapour. The two terms Δ_2 and Δ_3 are calculated from Equation (6), requiring knowledge of gas viscosities and densities.

For nitrogen gas, the following equation for the viscosity [28] was used:

$$\eta(\mu\text{Pa s}) = 3.4092 + 5.4573 \cdot 10^{-2} T - 2.1494 \cdot 10^{-5} T^2 + 5.0704 \cdot 10^{-9} T^3. \quad (9)$$

The density will be that of N_2 at the filling temperature 25°C, viz., 1.105 mg/cm³.

Equation (6) has been used in all cases when correcting for the damping of the melt vapour, which at the temperatures involved consists mainly of the dimer Al_2Cl_6 . The viscosity of this gas was determined by completely evaporating a known amount of AlCl_3 in the oscillating cup. The following equation was obtained in the range 250–290°C;

$$\log_{10} \eta(\text{mPa s}) = -1.023 - 466.67/T \quad (10)$$

where T is the absolute temperature.

The accuracy of Equation (10) is low (the net Al_2Cl_6 gas damping in these experiments was only $\leq 3 \cdot 10^{-4}$), but acceptable for the purpose of calculating Δ_3 (cf. discussion). The equation is applied at temperatures well below 250°C, but this can be done with reasonable safety as the magnitude of the correction decreases rapidly with temperature. The small variation of gas viscosity with pressure can also be neglected.

Evaporation Corrections

Evaporation of melt within the closed cup will cause

1. reduced liquid level
2. damping due to melt vapour
3. change of composition.

These corrections affect the viscosity in several more or less interdependent ways, and must be calculated using iterative procedures.

The density of the Al_2Cl_6 vapour in equilibrium with the $\text{NaCl}-\text{AlCl}_3$ mixtures was obtained by combining the van der Waals equation and the pressure equation reported by Viola et al. [10, 11] (using successive approximations necessitated by accompanying composition and height changes). The error introduced by extrapolating their equations to the present experimental upper limit of 300°C may not be negligible. For the 80 mol-% AlCl_3 melt, the iterations did not converge at 300°C, and the evaporation

corrections were in this case extrapolated from those obtained at lower temperatures.

The density of the vapour over pure $\text{AlCl}_3(1)$ was calculated from the vapour pressure equation of Viola et al. [9] and the van der Waals equation of Viola et al. [10], and compared with the density equation given by King, Seegmiller et al. [32, 35]. The latter was preferred above 250°C ; below this temperature the difference was negligible for the purpose of calculating vapour damping corrections.

In the printout heading, Fig. 2, SAMPLE DENSITY, LIQ. HEIGHT CM and P VAPOUR TORR are the sample density in g/cm^3 , the liquid height (cylindrical part) in cm and vapour pressure, respectively, before correction for evaporation. The corrected values P TORR CORR., DENSITY CORR. and LIQ. CM CORR. are then given, together with the corrected composition % AlCl_3 CORR. and corrected gas head GAS CM CORR. The vapour density and viscosity are also printed out. It is seen, for instance, that the actual composition at 262.3°C is 79.72 mol-% AlCl_3 , or 0.28 mol-% lower than the weighed-in nominal composition 80 mol-% AlCl_3 . This composition change alone leads to about 2% increase in the viscosity (see discussion).

The calculated vapour damping correction is included in the printout as VAPOUR DAMPING $\times 10000$. This damping cannot be calculated with sufficient accuracy from the solutions given here when the kinematic viscosity (η/ρ) of the vapour becomes too high [29], as sometimes happened. Based on calculation of a maximum value with $x = 7$ it was, however, in each such case concluded that the vapour damping correction could be neglected.

Meniscus Correction

Fig. 3 shows the results of a series of water measurements at 25°C with different liquid levels in the flatcup. Measured viscosities are always high compared with the 0.8904 mPa s value of Swindells [36] and Swindells et al. [37], and increase drastically at low liquid heights. The effect is mainly due to surface curvature. This has been demonstrated by creating a non-wetting condition with

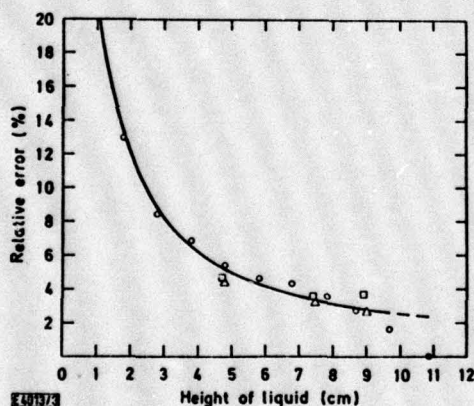


Fig. 3

Meniscus effect. Open circles: H_2O , flatcup partly filled. Filled circle: H_2O , flatcup completely filled. Open squares and triangles: KNO_3 , spherecup, 350°C and 375°C , respectively. Solid line calculated assuming an additional liquid height of 1.14 mm

a thin film of silicon grease, and repeating the experiments with varying liquid levels. An approximate mirror image of the Fig. 3 results was obtained, with low and rapidly decreasing viscosities at low levels.

Such meniscus errors can be by-passed by completely filling the flatcup, using Equations (5) and (6) with $k = 2$ and $h =$ half the height of the cup. This was done with water, giving the average value $\eta(25^\circ\text{C}) = 0.8903 \text{ mPa s}$, which is 0.01% below the Swindells value quoted above, and well within the 0.1°C temperature uncertainty.

It seems, however, nearly impossible to devise a means for filling the cup completely with molten salts, and the surface effect must be corrected for in other ways. A mathematical solution, if available, would require knowledge of the wetting and surface tension; data which are usually scarce. However, a satisfactory correction factor can be obtained by repeating measurements at different liquid heights since the meniscus effect for a given liquid is approximately independent of the liquid level. The method is too tedious to be routinely applied, but was used in control experiments as described below.

It has been found practical to express the meniscus effect as an adjustment to the calculated liquid height. Thus, the mean height correction at the nine water fillings of Fig. 3 was $+1.14 \text{ mm}$ ($\delta = +1.57 \cdot 10^{-4}$), with a standard deviation of 0.18 mm. The solid curve has been calculated assuming this constant height adjustment. Scattering in experimental results around the curve is probably due in large part to slight variations in the wetting of the nickel walls.

Molten KNO_3 was measured at three different heights in the spherecup. Results at 350°C and 375°C were corrected with $+1.14 \text{ mm}$ as for water. The resulting percentage changes in the viscosities, shown in Fig. 3, are in reasonable agreement with the water correction curve. The corrected values have also been compared with the expression recommended by Janz et al. for KNO_3 , [38]

$$\eta(\text{mPa s}) = 28.404 - 0.06752062 \cdot T + 0.4220783 \cdot 10^{-4} T^2 \quad (11)$$

Corrected spherecup values agree with Equation (11) within 0.6%.

The same empirical meniscus correction factor, expressed as a 1.14 mm increase in the liquid level, thus yielded corrected viscosities accurate to within about 1% for two rather different liquids. The applicability of this correction to the sodium chloroaluminate melts was tested with a 55 mol-% AlCl_3 melt. Spherecup results at two different fillings are given in Table 1. The observed values in the table were corrected by increasing the liquid height by 1.14 mm and recalculating the viscosities, which then agreed within 0.2%.

Table 1
Viscosity of NaCl-55 mol-% AlCl_3 , determined at two different fillings of the spherecup

Temp., $^\circ\text{C}$	Low level Height, cm	Viscosity, mPa s	Normal level Height, cm	Viscosity, mPa s
180.9	4.559	3.083	7.315	3.031
239.7	4.707	1.962	7.535	1.934
300.1	4.859	1.403	7.773	1.382

Although introduction of the meniscus correction hence appears to lead to improved viscosity values, the limitations involved are recognized and this correction is therefore kept separate from the otherwise fully corrected values reported below. The meniscus correction may improve as the result of future experimental and theoretical work. Meanwhile, the use of fairly long cups is advocated with reference to Fig. 3. Current work with the flatcup is carried out at liquid levels about 25 mm higher than the spherecup fillings.

Results

Seven NaCl- AlCl_3 mixtures ranging in composition from 50 mol-% to 80 mol-% AlCl_3 with 5 mol-% intervals were investigated using the spherecup. The temperature varied from 160°C to 300°C , generally in steps of about 20°C . More than four hundred single runs were performed. Table 2 summarizes results by listing the average value of (usually) 6 runs at each temperature and composition in the order performed. The relative standard deviations (SD) given are those of the means. The average SD is 0.13% (i.e., 0.32% for a single run).

Table 2
Viscosity of NaCl - AlCl₃ melts, average values. (Uncorrected viscosities; the use of the over-all correction factor 0.963 is recommended)

Composition, mol-% AlCl ₃	Temp., °C	kin visc., mPa s	SD, %
55.00	182.6	2.964	0.07
55.00	203.4	2.497	0.06
55.00	226.3	2.107	0.08
55.00	256.3	1.743	0.04
55.00	285.3	1.490	0.08
55.00	301.4	1.370	0.04
55.00	263.4	1.680	0.05
55.00	226.2	2.127	0.06
55.00	181.5	3.036	0.14
55.00	208.2	2.429	0.20
60.00	185.4	3.193	0.17
59.99	223.6	2.335	0.20
59.99	264.0	1.785	0.09
59.98	304.9	1.407	0.19
59.98	289.6	1.532	0.22
60.00	203.8	2.732	0.04
60.00	175.2	3.582	0.06
64.98	183.3	3.441	0.21
64.98	224.5	2.413	0.14
64.96	264.4	1.815	0.12
64.85	304.1	1.437	0.33
64.94	283.4	1.610	0.20
64.97	241.0	2.118	0.22
64.99	200.7	2.934	0.11
64.99	169.9	3.983	0.18
69.98	178.3	3.565	0.12
69.94 ^{*)}	226.8	2.307	0.14
74.92	195.3	2.638	0.10
74.88	223.3	2.064	0.11
74.80	261.6	1.541	0.13
74.74	283.8	1.331	0.13
74.63	306.3	1.165	0.32
74.85	241.7	1.777	0.30
79.86	199.5	1.993	0.13
79.77	242.1	1.390	0.13
79.62	285.1	1.038	0.09
79.50	302.7	0.922	0.09
79.72	262.3	1.189	0.13
79.82	220.2	1.630	0.16
69.97	179.9	3.501	0.09
69.95	219.4	2.419	0.14
69.90	260.1	1.785	0.06
69.82	300.0	1.386	0.09
69.86	281.6	1.551	0.12
69.92	239.4	2.068	0.08
69.96	205.5	2.736	0.21
69.97	191.5	3.107	0.03
50.0	180.1	2.812	0.11
50.0	225.3	2.006	0.24
50.0	263.3	1.584	0.13
50.0	304.1	1.284	0.22
50.0	281.5	1.439	0.20
50.0	242.2	1.796	0.26
50.0	200.4	2.352	0.05
50.0	161.0	3.317	0.07
50.0	169.3	3.063	0.10
50.0	193.1	2.496	0.04
50.0	212.2	2.168	0.19

^{*)} Experiment stopped due to later leakage.

Liquid heights in all NaCl-AlCl₃ experiments were close to 7.5 cm at the experimental mean temperature. It was found that the meniscus height correction of 1.14 mm gave a 3.2% viscosity increase, independent of the viscosities (in the present range) within 0.2%. All spherecup viscosities are furthermore 0.5% high due to

the approximation mentioned in footnote *). An over-all multiplication factor of 0.963 can therefore be applied to the entire body of experimental data in the sodium chloroaluminate system, except the viscosities of pure AlCl₃ obtained with the flatcup where only the meniscus correction factor 0.968 should be used.

In contrast, the percentage viscosity correction in the low-viscous liquid AlCl₃ varies with temperature (i.e., viscosity). Table 3a contains results obtained in this melt with the flatcup. Table 3b gives AlCl₃ viscosities after correcting the liquid height with +1.14 mm.

Table 3a

Viscosity of liquid AlCl₃, determined with the flatcup. The average value of six runs at each temperature is given, without meniscus corrections

1. Measuring series			2. Measuring series		
Temp., °C	Visc., mPa s	SD, %	Temp., °C	Visc., mPa s	SD, %
248.7	0.2093	0.09	269.0	0.1735	0.16
208.2	0.2997	0.08	285.8	0.1469	0.12
240.2	0.2252	0.19	209.0	0.2965	0.09
230.1	0.2472	0.06	225.0	0.2574	0.11
200.2	0.3210	0.14	261.8	0.1846	0.09
218.4	0.2735	0.06	278.9	0.1571	0.08
196.0	0.3334	0.07	233.8	0.2389	0.19
225.3	0.2569	0.08	212.6	0.2878	0.13
254.4	0.1979	0.11	196.0	0.3332	0.15

Table 3b

Viscosity of liquid AlCl₃, meniscus corrected Table 3a values. Standard deviations, see Table 3a

1. Measuring series		2. Measuring series	
Temp., °C	Viscosity, mPa s	Temp., °C	Viscosity, mPa s
248.7	0.2047	269.0	0.1695
208.2	0.2923	285.8	0.1436
240.2	0.2201	209.0	0.2885
230.1	0.2414	225.0	0.2507
200.2	0.3129	261.8	0.1802
218.4	0.2669	278.9	0.1535
196.0	0.3249	233.8	0.2328
225.3	0.2508	212.6	0.2801
254.4	0.1936	196.0	0.3240

The experimental data have been fitted to expressions of the type

$$\eta = a \exp(b/T + c/T^2) \quad (12)$$

using the simplex method of Nelder and Mead as applied by Hertzberg [39]. The least square sum in η was used as a minimizing criterion. The actual model employed was

$$\eta = A \exp[B(1/T - 1/T_m) + C(1000/T - 1000/T_m)^m - (1000/T_m - 1000/T_m)^m] \quad (13)$$

where

1000/T_m = 1.75 (upper exp. temperature T_u ~ 571 K)

m = 2

T_m: Experimental mean temperature, K

T: absolute temperature, K

η : Viscosity in mPa s (= Nsm⁻² · 10⁻³ = 1 centipoise).

For the 80 mol-% AlCl₃ melt, viscosities exhibit Arrhenius behaviour within the experimental uncertainty:

$$\eta = A \exp[B(1/T - 1/T_m)] \quad (14)$$

Table 4
Parameters in Equations (13), (14) for the viscosity of NaCl–AlCl₃ and AlCl₃ melts, with standard deviations (SD). The relative SD(%) of η in the fit is also given

AlCl ₃ , mol-%	Temp. span, K	Exp. points	A	SD · 10 ³	B	SD	C	SD	T _m , K	Rel. SD %
50	434–578	64	2.037	2.6	1515	19	0.2515	0.030	494.85	0.66
55	454–575	65	2.049	2.5	1577	22	0.3092	0.040	504.15	0.52
60	448–578	53	2.179	4.9	1653	30	0.3999	0.057	505.75	0.78
65	456–578	55	2.289	2.8	1759	19	0.3593	0.032	503.85	0.55
70	452–573	49	2.141	1.6	1870	13	0.2766	0.025	507.95	0.31
75 ¹⁾	468–580	38	1.665	1.8	1929	20	0.2026	0.044	523.95	0.50
75 ²⁾	453–573	—	1.792	—	1969	—	0.1724	—	513.15	—
80 ¹⁾	472–576	36	1.290	2.4	2024	13	—	—	525.15	0.93
80 ²⁾	453–573	—	1.477	—	2073	—	—	—	505.15	—
100 ³⁾	469–528	54	0.2590	0.2	2850	41	–1.240	0.074	497.75	0.30
100 ⁴⁾	469–559	52	0.2228	0.2	2987	25	–1.469	0.056	514.35	0.45
100 ⁵⁾	469–559	106	0.2349	0.1	2942	22	–1.415	0.045	505.85	0.49

¹⁾ Nominal composition. ²⁾ Parameters corrected to their 75% and 80% values. ³⁾ Flatcup, 1. series. ⁴⁾ Flatcup, 2. series.

⁵⁾ Combined flatcup 1. and 2. series, meniscus corrected.

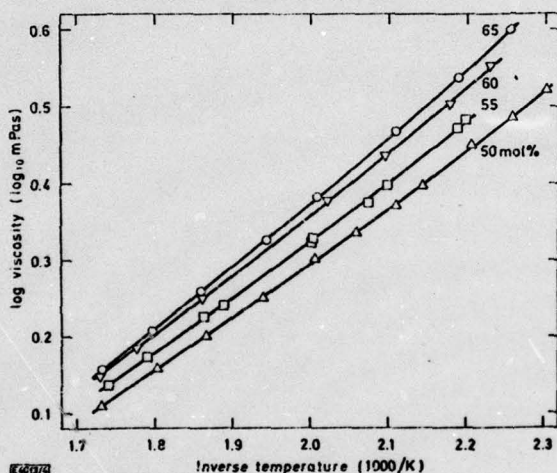


Fig. 4
Viscosity of NaCl–AlCl₃ melt mixtures, 50–65 mol-% AlCl₃ (nominal). Not corrected.

The parameters A, B, and C of Equations (13) and (14) were determined from the entire experimental material, not from the average values in Tables 2, 3a, and 3b. Results are given in Table 4 and Figs. 4 and 5. These data have not been corrected for the meniscus effect, with the exception of the combined 1. and 2. measuring series with the flatcup. Table 4 values for NaCl–AlCl₃ mixtures can be corrected by multiplying the given parameter A with 0.963 (see above).

Viscosity isotherms have been calculated from Equations (13), (14) and Table 4 parameters at 20°C intervals in the range 180–300°C, see Fig. 6.

The viscosities reported herein may be converted, if desired, to other liquid density bases using the relations

$$\Delta\eta(\%) = 1.02 \Delta\rho(\%) \quad (15)$$

for NaCl–AlCl₃ mixtures, and

$$\Delta\eta(\%) = 0.915 \Delta\rho(\%) \quad (16)$$

for pure AlCl₃. Viscosities so converted are correct within 0.1% for densities deviating not more than ~6%.

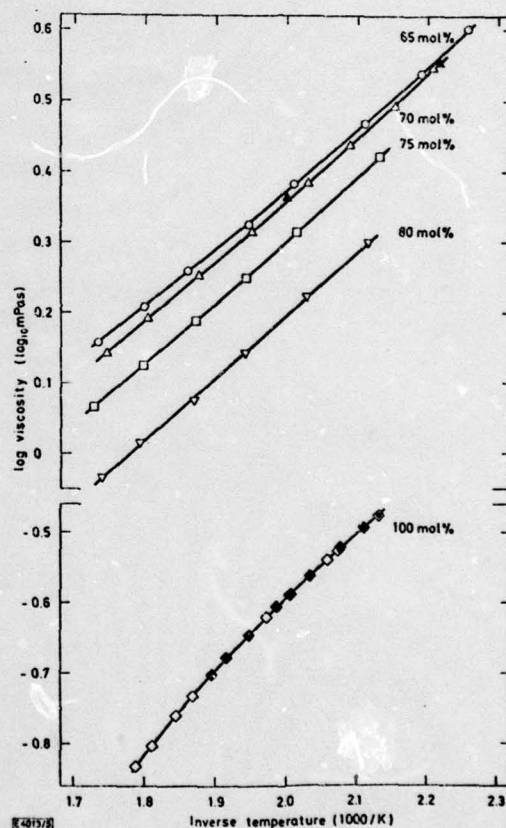


Fig. 5
Viscosity of AlCl₃ and NaCl–AlCl₃ melt mixtures, 65–80 mol-% AlCl₃ (nominal). Not corrected. Filled triangles: Series of 70 mol-% AlCl₃ interrupted due to later leakage. Filled and open diamonds: 1. and 2. measuring series in AlCl₃, respectively

Discussion

Evaluation of Accuracy

The viscometer is capable of measuring molten salt viscosities with an accuracy of 0.2% SD when equipped with a solid cylinder [28]. Estimated standard deviations of relevant

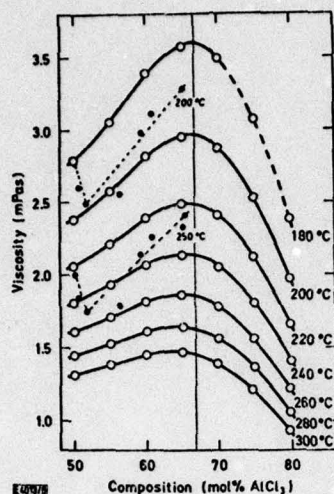


Fig. 6

Viscosity of NaCl-AlCl₃ melt mixtures vs. composition, not corrected. Broken curve at 180°C represent temperature extrapolated values. Filled circles: Kryagova [25]. The corresponding broken curves are as given by Kryagova. Vertical line: 66.7 mol-% AlCl₃. The curves are calculated from model, see discussion

viscometer parameters and their computer calculated effect on the viscosity are given in Tables 5a and 5b for the case of the cup. It is seen that similar accuracies can be approached only when height errors are eliminated, that is, by filling the cylinder completely. The result obtained in this way with water is, in fact, consistent with the accuracy claimed for solid cylinders.

Table 5a

Computer calculated effect on the viscosity of NaCl-AlCl₃ mixtures from perturbations in system parameters equal to one standard deviation. Basis NaCl - 75 mol-% AlCl₃ at 241.7°C, viscosity 1.787 mPa s. Total effects are given. Sphrecup

Parameter	Estimated SD		Rel. visc. change $\Delta\eta$, %
	Abs.	Rel., %	
Liquid height, meniscus corrected	0.2 mm	0.3	-0.6
Net log. decrement	$1.5 \cdot 10^{-5}$	0.1	0.2
Moment of inertia	1 g cm ²	0.08	0.2
Sample weight	50 mg	0.08	-0.2
Liquid density	1.5 mg cm^{-3}	0.1	0.1
Al ₂ Cl ₆ (g) density	3.5 mg cm^{-3}	10	0.1
Radius	3 μm	0.02	-0.06
Al ₂ Cl ₆ (g) viscosity	1.2 $\mu\text{Pa s}$	10	-0.04
Temp. (indirect)	0.5°C	-	-0.03
AlCl ₃ content	0.1 mol-%	-	-0.03
All periods	30 μs	0.002	~0
Total SD, $(\Sigma(\Delta\eta)^2)^{1/2}$			0.7

Table 5a is valid for sphrecup measurements of NaCl-AlCl₃ mixtures, while Table 5b applies to the later measurements with the flatcup in the very fluid aluminium chloride melt. Viscosity determinations using the flatcup will be discussed more fully in a later publication dealing with the viscosity of LiCl-AlCl₃ melts, in particular viscosities obtained from the ratio: period(g)/period(l).

These error tables show the "total" effect on the viscosity for a given change in the parameters, and should be judged

Table 5b

Computer calculated effect on the viscosity of AlCl₃, 196-286°C, from perturbations in system parameters equal to one standard deviation. (The abs. SD's are mean values). Total effects are given. The column headings $\eta(\text{damp.})$ and $\eta(\text{per.})$ refer to viscosities calculated from damping constants and period ratios, respectively. Flatcup

Parameter	Estimated SD		Rel. visc. change $\Delta\eta$, %	
	Rel., %	Abs.	$\eta(\text{damp.})$	$\eta(\text{per.})$
Liquid height, meniscus corrected	0.2	0.2 mm	-0.4	-0.4
Net log. decrement	0.15	$1.2 \cdot 10^{-5}$	0.3	~0
Sample weight	0.1	53 mg	-0.2	-0.2
Moment of inertia	0.05	0.5 g cm ²	0.1	0.1
Temp. (indirect)	-	0.5°C	-0.1	-0.1
Liquid density	0.1	1.2 mg cm^{-3}	0.1	0.1
Al ₂ Cl ₆ (g) viscosity	10	1.0 $\mu\text{Pa s}$	-0.06	~0
Radius	0.02	2.5 μm	-0.05	-0.05
Al ₂ Cl ₆ (g) density	0.1	$57 \mu\text{g cm}^{-3}$	~0	~0
Period, with liquid	0.001	20 μs	~0	-
Period increase	1.5	38 μs	-	3.0
Total SD, $(\Sigma(\Delta\eta)^2)^{1/2}$			0.6	3.1

with acumen. For instance, the isolated effect on the viscosity of the 3 μ radius error in Table 5a is -0.17%, as calculated directly from Equation (1). This is, incidentally, close to the solid cylinder value [28]. However, the associated change in the liquid level reduces the error to -0.06%, or only one-third of the "direct" effect. Another example is the uncertainty in the liquid density, which causes an error when introduced in the viscosity equations of the opposite sign to that given in Tables 5a and 5b. In this case, the related error in the liquid level more than compensates. The total effects given are considered to be of more practical interest than the isolated effects. The over-all standard deviation given at the end of each table has been calculated using the error distribution law.

The estimated SD's are, in part, higher than those assumed for the solid cylinder [28], especially for the moment of inertia and the net damping constant (in the tables given in terms of δ , that is, not in units of 2π). The moment of inertia, which was not redetermined prior to each series, changes somewhat when replacing gold seals and screws, and also because of weight losses due to corrosion. This will further affect the period, although only to the extent of influencing viscosities calculated from the period ratio. Greater care was taken in the period measurements with the flatcup than with the sphrecup for this reason.

The uncertainty in the net damping constant - the largest source of error next to the liquid height - is also greater than for the solid cylinder, for several reasons. The gas damping constant (and the period) cannot be checked immediately before runs in liquid as with the solid cylinder. Moreover, the accuracy of the N₂ displacement and the vapour damping correction terms (Equation (8)) depends on the acidity of the mixture and the temperature. In an extreme case (pure AlCl₃ in the flatcup), liquid expansion caused the gas space to be reduced from ~4 cm at the filling temperature 25°C to one-tenth of that value at the highest experimental temperature 286°C. The theoretical nitrogen pressure was then about 20 atm and the Al₂Cl₆ vapour pressure ~10 atm.

The nitrogen probably partly dissolves in the liquid, making the total pressure less than 30 atm. The over-all effect on the viscosity is difficult to estimate, but the calculated N_2 displacement correction possibly becomes too large.

Evaporation causes a loss in the liquid damping due to the reduction in liquid height, and also an accompanying increase in the Al_2Cl_6 vapour damping. Although each of these corrections may amount to several percent, it is noteworthy that their signs are opposite and that their numerical values were found to be about equal. There is thus, under present conditions, a large degree of compensation involved when a thin layer of liquid is transformed into a longer column of gas.

Composition errors are small, but care should be taken not to confuse nominal and actual concentrations. The viscosity isotherms in Fig. 6 were used to extrapolate viscosities to the nominal concentrations for the two melts in which composition changes due to evaporation is of importance (at 75 mol-% and 80 mol-% $AlCl_3$). The corrected A, B, and C parameters of Table 4 were determined from extrapolated viscosities. The concentrations indicated in Figs. 4 and 5 are nominal, but the qualitative trend of the curves does not change appreciably if corrected (extrapolated) viscosities are plotted instead.

The uncertainty in the liquid density, 0.1%, is that given by Fannin et al. [31]. Their density expression for NaCl– $AlCl_3$ mixtures has been extrapolated to include the 80 mol-% $AlCl_3$ melt in this work. Equations (15), (16) may be used to correct viscosities if improved densities become available. A 10% standard deviation in the $Al_2Cl_6(g)$ densities has been assumed because of the considerable temperature extrapolation of the equations given by Viola et al. [10, 11]. For $AlCl_3(l)$, the 0.1% SD given by King and Seegmiller [32] applies.

The uncertainty in the temperature readings is taken as 0.5°C SD (approx. 1°C max. error) for thermocouples calibrated as described above. The resultant error in Tables 5a, b is indirect, caused primarily by the influence of temperature changes on liquid density and liquid height. The potential error due to the temperature coefficient of viscous flow can be much higher, e.g., ~0.5% for a 0.5°C change at 240°C in liquid $AlCl_3$.

Compared to solid cylinder type experiments, radius errors are of much less importance with the cup. Some corrosion of the spherecup took place during the measuring series in the sodium chloroaluminate system, resulting in a radius increase of 5 μm , which is negligible according to Table 5a.

The dimensions of the cup were measured with the same accuracy (using the same equipment) as our platinum solid cylinder [28], i.e., 1 μm . An interesting comparison with the microscopically measured radius was furnished from the viscosity measurements with the flatcup completely filled with water. A mean radius, calculated from the known amount of water, the height of the water column and the density, differed by less than 1 μm from the measured value.

The deviation in the liquid height is taken as the ~0.2 mm SD found for water in the study of meniscus effects (cf. above). This estimate presupposes that the meniscus correction factor given earlier has been applied.

Fig. 7 gives the results obtained in $AlCl_3$ with the two type of cups. The spherecup values are superseded in accuracy by flatcup viscosities, but have been included to show the comparatively small effect of changing the oscillating vessel, introducing an entirely different mathematical analysis, increasing the liquid height with up to 65% and reducing the gas head from 3–4 cm to a few mm. The furnace core/heating element was also changed. The curvature is virtually identical, with spherecup results being about 1% high. The most likely causes of this discrepancy in the highly fluid $AlCl_3$ liquid are imperfect meniscus and evaporation corrections, the uncertainty in the gas damping correction term, and perhaps also slight temperature errors.

Comparison with Reported Results

Kryagova [25] measured NaCl– $AlCl_3$ viscosities from 50.2% to 65.5 mol-% $AlCl_3$ in the temperature range 200–300°C, using a capillary method. The viscosity isotherms at 200°C and 250°C are included in Fig. 6. Disregarding the unrealistic minimum at approximately 50 mol-% $AlCl_3$, the Kryagova results are about 10–20% high compared with present data.

Nisel'son and Sokolova [23] measured liquid $AlCl_3$ with an improved Martin capillary viscometer from the melting point to 276°C. Their results are included in Fig. 7. Further

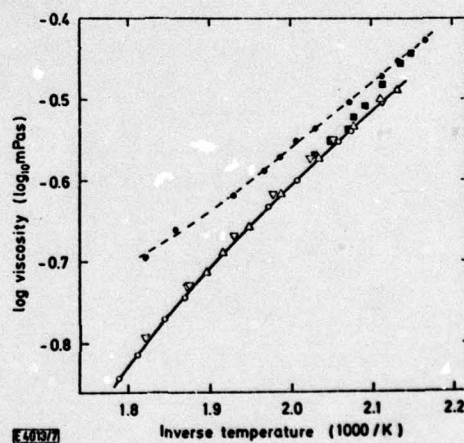


Fig. 7

Viscosity of pure $AlCl_3$. Filled circles and broken curve from Nisel'son and Sokolova [23]. Filled squares: Kleinschmit [24]. Triangles, apex downwards: This work, corrected spherecup results. Triangles apex upwards and open circles: This work, meniscus corrected flatcup results, 1. and 2. measuring series, respectively

included in Fig. 7 are the values of Kleinschmit [24], obtained in the narrow temperature span 192.5–220°C. Kleinschmit employed an oscillating vessel method involving certain calibrations.

The Nisel'son and Sokolova curve is slightly concave upwards, in contrast to present measurements. Agreement between the two investigations is fairly good in the low temperature range, where the Nisel'son and Sokolova result

is 8% high at 196°C. The authors obtained the following equation from a least squares fit

$$\eta(\text{mPa s}) = 3.602 \cdot 10^{-1} - 2.899 \cdot 10^{-3} \cdot \Delta t + 1.232 \cdot 10^{-5} (\Delta t)^2 \quad (17)$$

where $\Delta t = t - 192.5$ and t denotes °C. The range of validity is stated to be from the melting point, given as 192.5°C, to 276°C.

The two-term equation given by Boston [1] in his review of the Niselson and Sokolova work is erroneous, yielding viscosities 58% of the Equation (17) value at 276°C.

Kleinschmitt values are intermediate, but with a high temperature coefficient.

Outline of Viscosity Model for NaCl–AlCl₃ Melts

No existing theory on the molecular mechanism for viscous flow will give an adequate description of the highly complex acid sodium chloroaluminate system. We avoid any discussion of the viscosity as a property and take instead an empirical approach, later to be extended to other systems in this new series of viscosity determinations of complex-forming liquids.

The single salts LiCl, NaCl, KCl, RbCl, and CsCl all exhibit Arrhenius behaviour [28, 40]. In particular, the salts NaCl [28] and NaF [41] were investigated with the present viscometer and found to conform to the Arrhenius expression within 0.05% SD and 0.03% SD, respectively. The concept of activation energy for viscous flow is dubious, especially for processes not taking place at constant volume, and it is not our intention to support this concept. We do, however, find it significant that the Arrhenius rule is rigidly adhered to in non-complexing, bona fide salts like NaCl, while it is definitely not obeyed in NaCl–AlCl₃ mixtures (see below), which are known from other evidence to contain several species in chemical equilibrium. This distinction seems to become even clearer as work progresses in other systems.

In the NaCl–AlCl₃ system, viscosities follow approximately the Arrhenius temperature dependency in the high-temperature region, but deviate at low temperatures in the direction of higher viscosities (Table 4, Figs. 4, 5) with the exception of the 80 mol-% AlCl₃ melt. The curvature of the AlCl₃ plot is opposite to that of the mixtures and, in fact, to any melt so far measured in the present series of viscosity investigations.

Applying the tentative empirical rule expressed above, these observations indicate formation of complexes in the NaCl–AlCl₃ mixtures. At high temperatures, the number of species present seems reduced, and one species may dominate. The implication of the positive deviation from the Arrhenius rule at low temperatures is that the viscosity of the low-temperature species is more temperature sensitive ("activation energy" higher) than the presumably less complex high-temperature species. This seems reasonable, and is also consistent with the increased slopes of the curves at higher AlCl₃ concentrations, where higher complexes are likely to form (see below).

The AlCl₃ melt consists mainly of the dimer Al₂Cl₆ over the 196–286°C range investigated in this work [1], and the

unusual curvature is hence not likely to be due to shifting chemical equilibria (dissociation into AlCl₃). Also, according to the preceding argument, any significant increase in monomer concentration at higher temperatures would have resulted in a curvature opposite to that found. However, the observed negative deviation from Arrhenius can be expected as the critical point is approached. For AlCl₃, the critical temperature is 355.2°C [35], or only 69.4°C above our highest experimental temperature.

Considerably more information on the melt structure is obtained from the viscosity isotherms in Fig. 6. The general trends in the isotherms will first be described qualitatively, and a quantitative description will then be developed.

The major structural elements in acid chloroaluminate melts are known from Raman spectroscopy [5–8] to be AlCl₄[−], Al₂Cl₇[−], and Al₂Cl₆. Minor amounts of higher Al–Cl polymers, e.g. Al₃Cl₁₀[−], are probably also present at high AlCl₃ contents. The viscosity of the univalent species is expected to increase with each added AlCl₃-group, while the covalent Al₂Cl₆ liquid is known to be very fluid. The NaCl–AlCl₃ mixture will hence become more viscous as Al₂Cl₇[−] is formed by addition of AlCl₃. At the low temperature of 180°C a maximum in the viscosity is observed close to the composition 67 mol-% AlCl₃, corresponding to undissociated Al₂Cl₇[−]. The viscosity maximum is less pronounced and shifts markedly towards lower contents of AlCl₃ at higher temperatures due to a decreased stability of Al₂Cl₇[−].

There is an initial negative deviation from linearity on the left side of the maximum. This negative deviation is typical for mixtures of liquids with low molecular weights, and is commonly described by the Arrhenius mixing rule which implies additive activation energies of viscous flow [22]:

$$\ln \eta = \sum X_i \ln \eta_i. \quad (18)$$

A similar behaviour is not observed for $X_{\text{AlCl}_3} > 0.67$, at least not until the miscibility limit at $X_{\text{AlCl}_3} = 0.8$ is reached, which may be regarded as circumstantial evidence for the additional presence of the trimer Al₃Cl₁₀[−], already proposed from Raman spectra.

We now attempt to rationalize the NaCl–AlCl₃ viscosities by applying Equation (18) to a four-species model comprising AlCl₄[−], Al₂Cl₇[−], Al₃Cl₁₀[−], and Al₂Cl₆, with the expectation that this model will be more easily established than a purely parametrical model. In a strict sense the viscosity of, say Al₂Cl₇[−], is that of Al₂Cl₇[−] + Alk⁺.

Mathematical Formulation of Model

$$2\text{Al}_2\text{Cl}_7 = 2\text{AlCl}_4 + \text{Al}_2\text{Cl}_6 \quad (19)$$

$$X_4^2 X_6 / X_7^2 = K_7 = A_7 \exp(B_7/T)$$

$$2\text{Al}_3\text{Cl}_{10} = 2\text{Al}_2\text{Cl}_7 + \text{Al}_2\text{Cl}_6 \quad (20)$$

$$X_7^2 X_6 / X_{10}^2 = K_{10} = A_{10} \exp(B_{10}/T)$$

$$\text{Mol AlkCl: } n_{\text{AlkCl}}^0 = n_4 + n_7 + n_{10} \quad (21)$$

$$\text{Mol AlCl}_3: n_{\text{AlCl}_3}^0 = n_4 + 2n_7 + 3n_{10} + 2n_6 \quad (22)$$

$$1 \text{ mol mixture: } 1 = n_{\text{AlkCl}}^0 + n_{\text{AlCl}_3}^0 \quad (23)$$

Stoichiometric mol

$$\text{fraction of AlCl}_3: X^0 = n_{\text{AlCl}_3}^0 / (n_{\text{AlCl}_3}^0 + n_{\text{AlCl}}^0) = n_{\text{AlCl}_3}^0 \quad (24)$$

(Notation according to the number of Cl atoms). The number of mols is denoted n . All concentrations are expressed as mol fractions of the Al-containing species [7], for example

$$X_4 = n_4 / (n_4 + n_7 + n_{10} + n_6). \quad (25)$$

The following implicit expression in terms of n_6 is then obtained from Equations (19)–(24).

$$\begin{aligned} (X^0 - 2n_6)((K_7 K_{10})^{\frac{1}{2}} + K_{10}^{\frac{1}{2}} f + f^2) + (X^0 - 1)((K_7 K_{10})^{\frac{1}{2}} \\ + 2K_{10}^{\frac{1}{2}} f + 3f^2) = 0 \\ f = (n_6 / (1 - X^0 + n_6))^{\frac{1}{2}}. \end{aligned} \quad (26)$$

Furthermore,

$$n_7 = K_{10}^{\frac{1}{2}} f (1 - X^0) / ((K_7 K_{10})^{\frac{1}{2}} + K_{10}^{\frac{1}{2}} f + f^2) \quad (27)$$

$$n_4 = K_7^{\frac{1}{2}} f^{-1} n_7 \quad (28)$$

$$n_{10} = K_{10}^{-\frac{1}{2}} f n_7. \quad (29)$$

The viscosity of the mixture is assumed to be described by the Arrhenius mixture rule, which for the proposed four-species model is

$$\ln \eta = (n_4 + n_7 + n_{10} + n_6)^{-1} \cdot (n_4 \ln \eta_4 + n_7 \ln \eta_7 + n_{10} \ln \eta_{10} + n_6 \ln \eta_6). \quad (30)$$

The viscosity of AlCl_4^- (η_4) is taken to be the experimental value for the 50 mol-% AlCl_3 melt (cf. Table 4):

$$\eta_4 = A \exp[B(1/T - 1/T_m) + C((1000/T - 1.75)^2 - (1000/T_m - 1.75)^2)] \quad (31)$$

$$T_m = 494.85, \quad A = 2.037, \quad B = 1515, \quad C = 0.2515.$$

Dissociation of AlCl_4^- is thereby neglected, although indicated by the deviation from a simple Arrhenius linearity between $\ln \eta$ and $1/T$.

The viscosities of the other species ($\eta_7, \eta_6, \eta_{10}$), or rather the preexponential and exponential factors in the Arrhenius temperature expressions, are regarded as adjustable parameters:

$$\eta_i = \alpha_i \exp(\beta_i/T) \quad i = 6, 7, 10. \quad (32)$$

In these melts Al_2Cl_6 will be present in a partly ionic medium contrary to that in pure AlCl_3 , and we have chosen the viscosity of Al_2Cl_6 as a parameter rather than use the experimental value for $\text{AlCl}_3(l)$.

The experimental $\eta(T, X)$ -data were fitted to this four-species model, using the general model fit program of Hertzberg [39] mentioned earlier. Equations (13) and (14) were used with Table 4 parameters to generate a data grid similar to that in Fig. 6 (with the exception that viscosities extrapolated to their 75.0 mol-% and 80.0 mol-% values were used). Data points were spaced at 5 mol-%, 20°C intervals, in good imitation of the actual experimental program. The extrapolated values at 180°C for the 75 and 80 mol-% AlCl_3 melts were excluded, leaving 47 points to be fitted to Equation (30), with the species fractions as determined by Equations (26)–(29) and the viscosities by Equations (32).

Results are given in Table 6a. In the unrestricted model, the program was allowed to seek the best fit without restrictions on the adjustable parameters. Initial values (trial solutions) were selected with some care, however. A positive value of B_{10} was obtained, implying that the trimer $\text{Al}_3\text{Cl}_{10}$ increases in stability relative to Al_2Cl_7 with increasing temperature. This feature is at variance with chemical intuition, and in another fit the requirement $B_{10} < 0$ was therefore introduced (together with $B_7 < 1$), see Table 6a.

Table 6a

Parameters in viscosity models for $\text{NaCl}-\text{AlCl}_3$ melts. Viscosities calculated from these parameters should be multiplied with the over-all correction factor 0.963

Parameter	Unrestricted model (SD = 0.43%)	Restricted model B_7 and $B_{10} < 0$ (SD = 0.59%)
A_7	54.48	40.95
B_7	-845.6	-1339
A_{10}	$3.517 \cdot 10^{-3}$	$8.156 \cdot 10^{-2}$
B_{10}	819.6	-305.2
α_7	$9.380 \cdot 10^{-3}$	$1.398 \cdot 10^{-2}$
β_7	2617	2561
α_{10}	$9.849 \cdot 10^{-2}$	$7.164 \cdot 10^{-1}$
β_{10}	2547	1392
α_6	$7.566 \cdot 10^{-3}$	$9.022 \cdot 10^{-3}$
β_6	2011	1956

Table 6b

Equilibrium constants and species viscosities, calculated from Table 6a model parameters and Equations (26)–(31)

T , K	K_7	K_{10}	η_4 , mPa s	η_7 , mPa s	η_{10} , mPa s	η_6 , mPa s
Unrestricted model						
473	9.117	0.0199	2.381	2.372	21.477	0.531
573	12.455	0.0147	1.317	0.903	8.392	0.253
Restricted model (B_7 and $B_{10} < 0$)						
473	2.414	0.0428	2.381	3.140	13.591	0.564
573	3.957	0.0479	1.317	1.221	8.132	0.274

The standard deviation of η in the two fits is 0.43% and 0.59, respectively. The deviations of the viscosities in Table 4 ranges from 0.31% to 0.93% for the $\text{NaCl}-\text{AlCl}_3$ mixtures with an average deviation of 0.6%. In other words, the four-species model will in both fits reproduce $\text{NaCl}-\text{AlCl}_3$ viscosities within the experimental uncertainty, and a main objective is thereby fulfilled. Equations (19)–(22) and (26)–(29) together with Table 6a parameters provide thus a practical way of obtaining viscosities at any temperature and composition. Viscosities so computed should be multiplied by the over-all correction factor 0.963.

It is tempting to give a closer physico-chemical interpretation of the parameters in Table 6a, but the question of the physical reality of the model then arises. First, it may be noted that although the restricted and the unrestricted model are equally "probable", since the standard deviations in the fits are of the same order, equilibrium constants and viscosities of the assumed species differ considerably, see Table 6b. In an order-of-magnitude fashion, however, the viscosities have sensible values. The equilibrium constants are reasonable, and in the restricted model, both increase with temperature.

The qualitative trend of the viscosity isotherms that suggests the introduction of $\text{Al}_3\text{Cl}_{10}$ has already been described. Fig. 8 shows the result of removing the $\text{Al}_3\text{Cl}_{10}$ species from

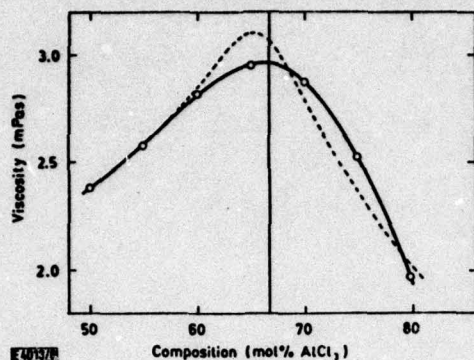


Fig. 8

Viscosity isotherms at 200°C for NaCl-AlCl₃ melt mixtures. Open circles: Experimental points. Solid curve: 4-species model. Broken curve: 3-species model

consideration by disregarding Equation (20) and putting $\eta_{10} = 0$ in Equations (21), (22), (25), thus arriving at a three-species model with only AlCl_4^- , Al_2Cl_7^- , and Al_2Cl_6 . According to the model fit program, the viscosity maximum is then displaced from 66.2 mol-% to 65.0 mol-% and the standard deviation of η in the fit increases by a factor of about 10. The change in the shape of the curve is also noteworthy. These rather drastic effects lend, in themselves, some support to the physical reality of the four-species model.

It would further be of interest to compare our parametrical, adjustable equilibrium constants K_7 and K_{10} (Table 6b) with reported values obtained by other means. Values for K_{10} have not been reported. Fannin et al. [14] assign the value 0.09 to K_7^* from electrochemical data obtained at 175°C with melts containing 71 mol-% AlCl_3 or less. Since the authors applied a three-species model, direct comparison with the present K_7 values becomes difficult. In the present case, for instance, the K_7 constant at 200°C changed from 2.4 to 0.002 (restricted model) when fitting the three-species model to the experimental data. The Fannin et al. value is approximately in the middle of this range.

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* The conversion of the data of Fannin et al. [14] is given by: $K_7 = 2K^0/K_7^2$.

VISCOSITY OF ACIDIC LITHIUM CHLOROALUMINATE MELTS

Final data report 28/2-1979

by

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The viscosity of acid lithium chloroaluminate melts has been determined at 5 mol% intervals from 50 mol% to 80 mol% AlCl_3 over the temperature range: liquidus - 300°C . The oscillating right-angular cup ("flatcup") method was used [1]. The experimental procedure for NaCl-AlCl_3 mixtures was essentially retained for the present LiCl-AlCl_3 melts, with the exception that corrections for vaporization could not be made due to the lack of vapour pressure data. Such effects were instead minimized by reducing the space between the liquid surface and the pressure-tight lid to about 5-10 mm. The length of the liquid column was then ~ 10 cm.

Results are given in Tables 1-9. The data points are given *in toto* in Tables 2-8, while Table 1 contains the average values at each temperature and composition. The results are always given in the order measured. The standard deviations (SD) in Tables 2-8 have been calculated from the SD in the mean damping constant for each run. The deviations given in Table 1 are the SD in the average viscosity values of the four runs usually carried out at each temperature.

[1] W. Brockner, K. Tørklep and H.A. Øye: "Viscosity of Aluminium Chloride and Acidic Sodium Chloroaluminate Melts", Ber. Bunsenges. Phys. Chem. 83 (1979) 1.

The following models were fitted to the individual results contained in Tables 2-8:

$$\eta = A \exp[B(1/T - 1/T_M)] \quad (1)$$

$$\eta = A \exp[B(1/T - 1/T_M) + C((1000/T - 1000/T_U)^m - (1000/T_M - 1000/T_U)^m)] \quad (2)$$

where

T: Temperature, K

T_M: Experimental mean temperature, K

1000/T_U: 1.70

m: 3

η : Viscosity, mPas ($= N \text{sm}^{-2} \cdot 10^{-3} = 1 \text{ centipoise}$)

The temperature dependencies of the 75 mol% and 80 mol% AlCl₃ melts were "linear" in the sense that fitting Equation (2) with varying $m > 1$ did not significantly improve the SD in the fit compared with Equation (1). For these two melts, Equation (1) applies. The parameters A, B and C are given in Table 9, with standard deviations. Also included in Table 9 are T_M, the standard deviations of the viscosity in the fit, the number of experimental points and the temperature span for each melt. (Note: the parameters m and 1000/T_U change according to the melt system - NaCl/AlCl₃, LiCl/AlCl₃ or ternary LiCl/NaCl/AlCl₃).

None of the viscosity data referred to above has been corrected for liquid surface curvature (the meniscus effect). This effect has been discussed in ref. [1], and further in ref. [2] for the ternary LiCl/NaCl/AlCl₃ melts. The equation for the meniscus correction factor obtained in ref. [2] applies also to the present binary LiCl/AlCl₃ melts:

$$\eta_{\text{corr.}}/\eta = 0.977 - 0.0011 \cdot \eta \quad (3)$$

[2]. K. Tørklep and H.A. Øye: "Viscosity of the Ternary System AlCl₃-LiCl-NaCl Containing Excess AlCl₃". Data report 28/2-1979.

Here, η is the experimentally observed viscosity and $\eta_{\text{corr.}}$ the meniscus-corrected value. For instance, the viscosity η of LiCl with 60 mol% AlCl₃ at 110.9°C is 10.64 mPas according to Table 1. The corrected value $\eta_{\text{corr.}}$ becomes 10.27 mPas.

Equation (3) was obtained using the general liquid height correction +1.14 mm [1], but because of the large range of viscosities in the LiCl/AlCl₃ and LiCl/NaCl/AlCl₃ melts, the viscosity dependence of the derived correction factor cannot be neglected as done in the NaCl/AlCl₃-investigation [1]. The constant correction factor 0.968 given in the previous data report of 8/3 1978 for LiCl/AlCl₃ melts should be disregarded, as it was based on viscosities and liquid column heights typical for NaCl/AlCl₃ mixtures.

The viscosities reported here may be converted, if desired, to other density bases using the relation

$$\Delta\eta(\%) = 0.947\Delta\rho(\%) \quad (4)$$

where $\Delta\rho(\%)$ is the percentage deviation from the densities used in this work (obtained from FJSRL). Viscosities so converted are correct within 0.1% for densities deviating up to 6%.

The accuracy of the oscillating cup method has been discussed extensively in ref. [1]. Table 10 summarizes the effect of the various sources of errors for the case of flat-cup filled with LiCl-AlCl₃ melts. The total estimated standard deviation in the accuracy is 0.5% (RMS), assuming that the meniscus effect has been corrected for.

A four-species viscosity model assuming the presence of AlCl₄⁻, Al₂Cl₇⁻, Al₃Cl₁₀⁻ and Al₂Cl₆ has been provisionally fitted to the obtained viscosities for binary LiCl/AlCl₃ melts in a restricted range of temperatures, cf. Appendix. The model is identical to that used for NaCl/AlCl₃ mixtures [1], and gives a standard deviation of 0.34% for the viscosity in the fit. The corresponding fit for NaCl/AlCl₃ was 0.43%.

Viscosity isotherms are given in Figure 1. (The Arrhenius temperature plots for the LiCl-AlCl₃ melts are part of Figure 1 in the data report of 20/2 1979 [2] for the system AlCl₃-LiCl-NaCl). The data points were calculated from Equations (1,2)

using Table 9 parameters. The differences between the provisional model in the Appendix and the experimental isotherms of Figure 1 are not visible in the 160-300°C temperature span. This model is satisfactory for interpolation purposes in the approximate range 160-300°C, 50-80 mol% AlCl₃. Work is in progress to obtain a refined model in which also lower-temperature viscosities can be included.

A three-species model in which the species Al₃Cl₁₀⁻ was "replaced" by two interaction parameters in the Arrhenius mixture equation was also tried. The standard deviation in the viscosity in the fit thereby reduced to 0.73%, which might be considered a significant deterioration. However, a discussion of the structure of LiCl/AlCl₃ melts is postponed to a final publication.

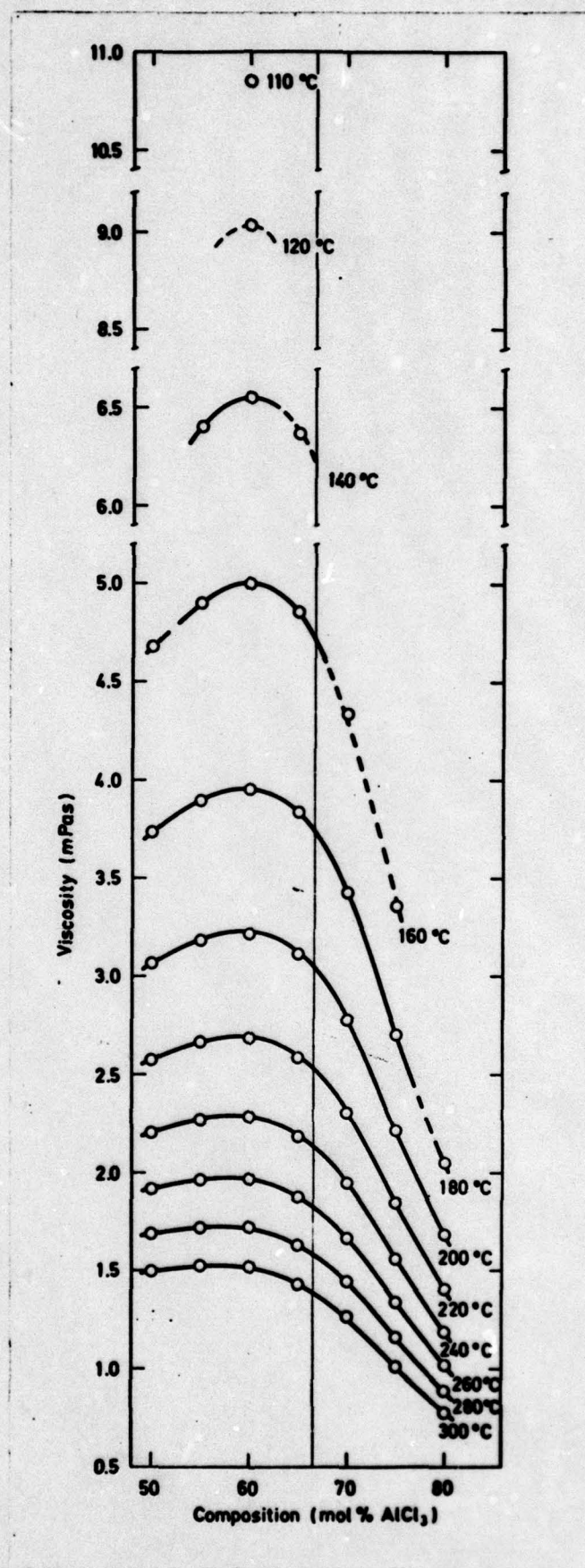


Fig. 1. Experimental viscosity isotherms for LiCl-AlCl_3 mixtures.

Table 1. Viscosity of LiCl-AlCl₃ melts, average values.

Composition, mol% AlCl ₃	Temp., °C	Mean visc., mPas	SD, %
50	268.9	1.813	0.05
	299.1	1.502	0.11
	235.6	2.275	0.07
	204.7	2.948	0.04
	173.6	3.998	0.02
	285.4	1.629	0.03
	253.1	2.003	0.04
	189.6	3.388	0.03
	226.1	2.453	0.04
	213.7	2.704	0.04
	180.9	3.682	0.08
	169.0	4.207	0.03
	164.6	4.433	0.01
55	278.9	1.734	0.09
	301.7	1.509	0.11
	239.8	2.273	0.04
	199.1	3.210	0.09
	259.3	1.973	0.05
	220.7	2.648	0.06
	179.0	3.937	0.10
	160.3	4.885	0.12
	140.7	6.338	0.08
60	301.0	1.505	0.04
	279.2	1.724	0.05
	260.8	1.955	0.03
	241.8	2.255	0.13
	179.9	3.958	0.02
	200.7	3.202	0.03
	220.4	2.679	0.02
	161.8	4.889	0.04
	140.8	6.464	0.06
	119.9	9.055	0.06
65	110.9	10.644	0.01
	301.2	1.421	0.06
	280.1	1.629	0.06
	259.3	1.881	0.05
	241.7	2.153	0.03
	220.1	2.580	0.06
	200.0	3.111	0.02
	180.0	3.836	0.03
	160.1	4.848	0.03
	144.5	5.965	0.03

(Table 1, cont'd)

Composition, mol% AlCl_3	Temp., $^{\circ}\text{C}$	Mean visc., mPas	SD, %
70	239.0	1.965	0.02
	280.3	1.439	0.12
	301.3	1.255	0.03
	260.7	1.657	0.05
	219.1	2.324	0.04
	198.1	2.828	0.03
	179.3	3.451	0.04
	170.0	3.839	0.03
75	239.0	1.572	0.05
	261.3	1.327	0.06
	299.6	1.012	0.04
	279.4	1.157	0.05
	219.8	1.836	0.02
	199.6	2.211	0.03
	179.4	2.728	0.02
80	199.9	1.685	0.10
	240.8	1.182	0.03
	260.2	1.017	0.06
	298.3	0.779	0.08
	280.3	0.880	0.06
	220.2	1.402	0.03
	189.0	1.871	0.03

Table 2. Viscosity of LiCl-50 mol% AlCl₃.

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
268.9	1.814	1
	1.816	1
	1.812	1
	1.812	2
	1.811	1
299.1	1.497	2
	1.504	1
	1.504	1
	1.502	1
235.6	2.271	2
	2.278	2
	2.278	2
	2.275	2
204.7	2.949	2
	2.946	3
	2.945	2
	2.950	3
	2.950	3
173.6	3.996	3
	3.999	3
	4.000	3
	3.995	3
	3.999	2
285.4	1.630	1
	1.628	1
	1.629	2
	1.630	1
253.1	2.001	2
	2.004	1
	2.002	2
	2.006	1
	2.003	2
189.6	3.389	2
	3.389	2
	3.391	2
	3.386	2
	3.385	3
226.1	2.454	2
	2.453	2
	2.450	2
	2.454	2

To be continued

(Table 2, cont'd)

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
213.7	2.704	2
	2.707	3
	2.701	2
	2.704	3
	2.705	3
180.7	3.671	4
	3.687	2
	3.682	3
	3.686	3
	3.685	2
169.0	4.211	3
	4.205	3
	4.208	3
	4.205	3
	4.205	3
164.6	4.433	3
	4.433	4
	4.435	4
	4.433	3

Table 3. Viscosity of LiCl-55 mol% AlCl₃.

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
278.9	1.731	2
	1.732	1
	1.738	2
	1.734	2
301.7	1.505	1
	1.508	2
	1.512	2
	1.509	2
239.8	2.275	4
	2.275	3
	2.271	2
	2.273	3
199.1	3.217	6
	3.211	3
	3.203	3
	3.208	4
259.3	1.971	3
	1.975	4
	1.972	4
	1.972	2
220.7	2.647	3
	2.645	3
	2.651	3
	2.651	4
179.0	3.949	4
	3.935	3
	3.932	3
	3.932	4
160.3	4.869	4
	4.886	4
	4.893	5
	4.893	5
140.7	6.324	5
	6.341	6
	6.343	5
	6.345	5

Table 4. Viscosity of LiCl-60 mol% AlCl₃.

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
301.0	1.507	1
	1.506	2
	1.504	1
	1.504	1
279.2	1.726	2
	1.723	1
	1.726	1
	1.723	1
260.8	1.955	2
	1.954	1
	1.956	2
	1.956	2
241.8	2.249	2
	2.251	2
	2.250	2
	2.250	2
179.9	3.960	2
	3.959	2
	3.957	5
	3.957	3
200.7	3.203	2
	3.199	2
	3.203	2
	3.203	2
220.4	2.679	2
	2.679	2
	2.681	2
	2.678	2
161.8	4.889	3
	4.888	3
	4.894	3
	4.885	4
140.8	6.470	6
	6.452	4
	6.468	4
	6.467	5
119.9	9.039	6
	9.059	6
	9.060	6
	9.063	6
110.9	10.642	9
	10.645	8
	10.645	7

Table 4. Viscosity of LiCl-60 mol% AlCl₃.

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
301.0	1.507	1
	1.506	2
	1.504	1
	1.504	1
279.2	1.726	2
	1.723	1
	1.726	1
	1.723	1
260.8	1.955	2
	1.954	1
	1.956	2
	1.956	2
241.8	2.249	2
	2.251	2
	2.250	2
	2.250	2
179.9	3.960	2
	3.959	2
	3.957	5
	3.957	3
200.7	3.203	2
	3.199	2
	3.203	2
	3.203	2
220.4	2.679	2
	2.679	2
	2.681	2
	2.678	2
161.8	4.889	3
	4.888	3
	4.894	3
	4.885	4
140.8	6.470	6
	6.452	4
	6.468	4
	6.467	5
119.9	9.039	6
	9.059	6
	9.060	6
	9.063	6
110.9	10.642	9
	10.645	8
	10.645	7
	10.643	6

Table 5. Viscosity of LiCl-65 mol% AlCl₃.

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
301.2	1.423	1
	1.421	1
	1.420	1
	1.419	1
280.1	1.628	2
	1.630	1
	1.629	1
	1.626	1
259.3	1.880	3
	1.880	1
	1.882	1
	1.884	2
241.7	2.153	3
	2.155	1
	2.153	2
	2.153	2
220.1	2.575	2
	2.581	1
	2.581	2
	2.582	2
200.0	3.110	3
	3.112	2
	3.109	2
	3.112	3
180.0	3.838	3
	3.834	3
	3.837	3
	3.833	4
160.1	4.847	6
	4.845	3
	4.851	3
	4.850	3
144.5	5.966	5
	5.970	4
	5.964	3
	5.960	4

Table 6. Viscosity of LiCl-70 mol% AlCl₃.

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
239.0	1.965	3
	1.965	2
	1.966	5
	1.964	1
280.3	1.535	2
	1.438	3
	1.440	1
	1.443	1
301.3	1.255	1
	1.256	1
	1.255	1
	1.254	1
260.7	1.659	2
	1.657	2
	1.655	2
	1.656	2
219.1	2.321	3
	2.324	1
	2.325	3
	2.324	2
198.1	2.876	2
	2.827	2
	2.828	2
	2.829	2
179.3	3.456	2
	3.450	2
	3.450	2
	3.450	2
170.0	3.837	3
	3.839	3
	3.838	4
	3.842	3

Table 7. Viscosity of LiCl-75 mol% AlCl₃.

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
239.0	1.571	1
	1.574	1
	1.573	1
	1.571	1
261.3	1.328	1
	1.329	1
	1.328	1
	1.326	1
299.6	1.013	1
	1.012	1
	1.011	1
	1.012	1
279.4	1.158	1
	1.156	1
	1.156	1
	1.156	1
219.8	1.837	1
	1.836	1
	1.836	1
	1.836	1
199.6	2.212	1
	2.210	1
	2.210	1
	2.212	1
179.4	2.727	2
	2.728	2
	2.728	1
	2.726	2

Table 8. Viscosity of LiCl-80 mol% AlCl₃.

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
199.9	1.690	3
	1.684	1
	1.684	1
	1.683	1
240.8	1.181	2
	1.182	1
	1.182	1
	1.183	1
260.2	1.019	2
	1.017	1
	1.017	1
	1.016	1
298.3	0.779	1
	0.779	1
	0.781	1
	0.780	1
280.3	0.880	1
	0.879	1
	0.881	1
220.2	1.401	1
	1.402	2
	1.402	1
	1.401	1
189.0	1.870	1
	1.871	1
	1.873	1
	1.871	1

Table 9. Parameters in Equations (1, 2) for the viscosity of LiCl-AlCl_3 melts, with standard deviations (SD). The relative SD (%) of η in the fit is also given.

AlCl_3 , mol%	Temp. span, K	Exp. points	A	$\text{SD} \cdot 10^3$	B	SD	C	$\text{SD} \cdot 10^3$	TM, K	Rel. SD, %
50	437-573	60	2.606	1.4	1869	7.1	0.3820	15	491.65	0.27
55	413-575	36	2.666	1.2	1937	4.5	0.3435	6.1	493.05	0.16
60	393-574	40	2.916	1.2	1975	3.6	0.3441	3.4	483.75	0.15
65	417-574	36	2.566	0.6	2058	2.4	0.2759	3.5	493.95	0.11
70	443-575	32	2.095	0.8	2086	4.6	0.2422	11	504.15	0.16
75	453-573	28	1.560	1.6	2135	5.8	-	-	512.85	0.43
80	462-572	28	1.177	1.6	2114	1.8	-	-	514.35	0.13

Table 10. Computer calculated effect on the viscosity of LiCl-AlCl₃ mixtures from perturbations in system parameters equal to one standard deviation. Basis LiCl - 65 mol% AlCl₃ melt at 220.1°C, viscosity 2.582 mPas. Total effects are given. Flatcup.

Parameter	Estimated SD		Rel.visc.change,%	
	Abs.	Rel.,%	η (damp.)	η (per.)
Liquid height, meniscus corrected	0.2 mm	0.2	-0.5	-0.4
Sample weight	50 mg	0.07	-0.2	-0.1
Net log. decrement	$1.5 \cdot 10^{-5}$	0.05	0.1	~0
Moment of inertia	0.5 gcm ²	0.05	0.1	0.1
Liquid density	1.5 mgcm ⁻³	0.1	0.1	0.1
Radius	3 μ m	0.02	-0.07	-0.05
Temp. (indirect)	0.5°C	-	-0.03	-0.03
Comp.; AlCl ₃ content	0.1 mol%	-	-0.03	-0.02
Period, with liquid	30 μ s	0.0015	~0	0.60
Period, empty (N ₂)	30 μ s	0.0015	~0	0.60
Total SD, $(\sum (\Delta\eta)^2)^{1/2}$			0.5	1.0

APPENDIX

The four-species viscosity model provisionally applied to the present data is discussed in ref. [1] and defined by Equations (19-30) and Equation (32) in that publication. The species assumed are AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$ and Al_2Cl_6 .

The data grid used in the model fitting is that of Figure 1 excluding the points at 110, 120 and 140°C, *i.e.*, 55 points in the range 160-300°C, 50-80 mol% AlCl_3 (the 160°C, 80% point was deleted because of the excessive temperature extrapolation involved). The data points were calculated from Equations (1,2) using Table 9 parameters.

The resulting model parameters are given in Table A1. The use of the model to calculate viscosities at any given combination of temperature and composition is described in the following.

First, the stoichiometric constants K_7 and K_{10} of the model is obtained for the considered temperature using the equations (*cf.* Table A1)

$$K_7 = 1.248 \exp(-1776/T) \quad (\text{A1})$$

$$K_{10} = 0.08726 \quad (\text{A2})$$

where T is temperature Kelvin. The model is restricted in the sense that the temperature dependency of K_{10} is disregarded (introducing an exponential term in Equation (A2) will not improve the total fit and it is hence redundant).

The number of mols of Al_2Cl_6 - n_6 - is then computed by numerical methods from the following expression, where x^0 is the mol fraction of AlCl_3 in the $\text{LiCl}/\text{AlCl}_3$ mixture.

$$(x^0 - 2n_6) ((K_7 K_{10})^{\frac{1}{2}} + K_{10}^{\frac{1}{2}} f + f^2) + (x^0 - 1) ((K_7 K_{10})^{\frac{1}{2}} + 2K_{10}^{\frac{1}{2}} f + 3f^2) = 0 \quad (\text{A3})$$

$$f = (n_6 / (1 - x^0 + n_6))^{\frac{1}{2}}$$

The number of mols of the other species are given by

$$n_7 = K_{10}^{\frac{1}{2}f(1-x^0)} / ((K_7 K_{10})^{\frac{1}{2}} + K_{10}^{\frac{1}{2}f+f^2}) \quad (A4)$$

$$n_4 = K_7^{\frac{1}{2}f-1} n_7 \quad (A5)$$

$$n_{10} = K_{10}^{-\frac{1}{2}f} n_7 \quad (A6)$$

The viscosities of the component species $Al_2Cl_7^-$, $Al_3Cl_{10}^-$ and Al_2Cl_6 are then calculated from Arrhenius equations using Table A1 preexponential and exponential factors:

$$\eta_7 = 0.03591 \exp(2232/T) \quad (A7)$$

$$\eta_{10} = 0.03524 \exp(2007/T) \quad (A8)$$

$$\eta_6 = 0.009139 \exp(2115/T) \quad (A9)$$

In the particular case of $AlCl_4^-$, the viscosity η_4 of this species is taken to be the experimental value for the 50 mol% $AlCl_3$ melt (cf. Table 9):

$$\eta_4 = 2.606 \exp[1869(1/T - 1/491.65) + 0.3820((1000/T - 1.70)^3 - (1000/491.65 - 1.70)^3)] \quad (A10)$$

Finally, the mol numbers and viscosities of the various species as computed above are introduced in the following Arrhenius mixture equation to give the viscosity η^* of the $LiCl/AlCl_3$ mixture at the considered temperature and composition:

$$\ln \eta = (n_4 + n_7 + n_{10} + n_6)^{-1} \cdot (n_4 \ln \eta_4 + n_7 \ln \eta_7 + n_{10} \ln \eta_{10} + n_6 \ln \eta_6) \quad (A11)$$

The standard deviation of η in this fit is 0.34%.

The model is provisional. In order to include low-temperature experimental viscosities at 110-140°C it seems necessary to introduce second-order terms in the Arrhenius equations (A7), (A8) and (A9). Furthermore, the viscosities should be corrected for the viscosity-dependent meniscus effect using Equation (3) before fitting the model. Another point of interest

* Not corrected for the meniscus effect.

is that the cup might no longer be considered "large" at the highest viscosities measured. This possible source of error (negative in sign) will be checked using the exact form of the cylinder equations, but the error is not expected to exceed the experimental uncertainty of 0.5%.

Table A2 lists stoichiometric constants and species viscosities at 200°C, calculated from the models for NaCl/AlCl₃ and LiCl/AlCl₃.

Table A1. Parameters in a four-species viscosity model for LiCl-AlCl₃ binary melts. Viscosities calculated from the model should be multiplied with the appropriate meniscus correction factor obtained from Equation (3). Restricted model ($B_{10}=0$).

Parameter	Value
A ₇	1.248
B ₇	-1776
A ₁₀	0.08726
α ₇	0.03591
β ₇	2232
α ₁₀	0.03524
β ₁₀	2007
α ₆	0.009139
β ₆	2115

Table A2. Calculated stoichiometric constants and species viscosities (mPas) at 200°C from fitted models for NaCl/AlCl₃ and LiCl/AlCl₃ binary mixtures.

Parameter	NaCl/AlCl ₃	LiCl/AlCl ₃
K ₇	2.4167	0.0293
K ₁₀	0.0428	0.0876
η ₄	2.3790	3.0625
η ₇	3.1347	4.0168
η ₁₀	13.578	2.4506
η ₆	0.5632	0.7984

VISCOSITY OF THE TERNARY SYSTEM
 AlCl_3 -LiCl-NaCl CONTAINING EXCESS AlCl_3

Final data report 20/2-1979

by

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Viscosities in the ternary system AlCl_3 -LiCl-NaCl have been measured using the same experimental technique as for the binary LiCl- AlCl_3 melts [1]. The chemicals for the melts containing 50 mol% AlCl_3 had to be purified with extraordinary care to avoid precipitates from being formed. The aluminium chloride was distilled three times, the lithium chloride recrystallized thrice after the usual HCl treatment and filtering.

Experimental temperatures varied from the apparent liquidus temperature to 300°C, measured compositions are those agreed upon in the Memorandum of agreement [2] and shown in Figure 1 in the Final report of 28/2-1979.

Results are given in Tables la-ld, and in Tables A1-A10 in the Appendix. Tables la-ld given mean viscosities and their uncertainties (expressed as the standard deviation SD

[1] K. Tørklep and H.A. Øye: "Viscosity of Acidic Lithium Chloroaluminate Melts". Data report 28/2-1979.

[2] L.A. King and H.A. Øye: "Memorandum of agreement", March 9, 1978.

in the mean) at each temperature and composition. Tables A1-A10 contain the entire experimental material. The uncertainties in these tables were derived from the SD in the mean damping constant at each run.

The following model was fitted to the individual results given in Tables A1-A10:

$$\eta = A \exp[B(1/T - 1/T_M) + C((1000/T - 1000/T_U)^m - (1000/T - 1000/T_U)^m)] \quad (1)$$

Here,

T: Temperature, K
 T_M: Experimental mean temperature, K
 1000/T_U: 1.75
 m: 3
 η: Viscosity in mPas (=cP)

The temperature dependency of the 80-10-10 mol% AlCl₃-LiCl-NaCl melt was linear in the sense that the parameter C could be put equal to zero without any significant increase in the SD of the fit. (The same linearity exists in mixtures of NaCl with 80 mol% AlCl₃ and in LiCl with 75 and 80 mol% AlCl₃).

The parameters A, B, C and T_M are given in Table 2 for all investigated ternary melts. Also included in this table are the experimental temperature ranges, the number of data points, and the uncertainties in A, B, C and η.

In the data report for binary LiCl/AlCl₃ melts [1], the following expression is given for converting viscosities to other density bases than used by us:

$$\Delta\eta(\%) = 0.947\Delta\rho(\%) \quad (3)$$

This equation is valid also for ternary AlCl₃-LiCl-NaCl mixtures. As for LiCl/AlCl₃ melts, viscosities converted according to Equation (3) will be correct within 0.1% for densities deviating up to 6% from those employed in this

work. (The corresponding equation for binary NaCl/AlCl₃ melts [3] differs somewhat from Equation (3), mainly because of the lower liquid heights in that system).

We have used ternary densities as reported by FJSRL. For melts with 50 mol% AlCl₃, polynomials fitted to experimental data were used. At the time the other ternary mixtures were investigated by us, experimental densities were not available. In these melts we employed instead an equation given by FJSRL which predicts ternary densities from the densities of the binaries NaCl-AlCl₃ and LiCl-AlCl₃. Comparison with experimental data for 50 mol% AlCl₃ melts, later also for 60 mol% AlCl₃ melts, showed a discrepancy of some 0.3-0.5% between predicted and experimental densities.

None of the data given above has been corrected for liquid surface curvature (the "meniscus effect"). The previously obtained liquid height correction [3] of +1.14 mm is assumed to apply also to the present melts. The effect on calculated viscosities is to a certain extent viscosity dependent, which cannot be neglected with the present wide range of viscosities. The expression for the viscosity-dependent meniscus correction factor becomes

$$\eta_{\text{corr.}} / \eta = 0.977 - 0.0011 \cdot \eta \quad (2)$$

where η is the measured viscosity and $\eta_{\text{corr.}}$ the meniscus-corrected value.

All viscosities given in Tables 1a-1d and A1-A10, or as calculated from Equation (1) with Table 2 parameters should be corrected using Equation (2). For instance, with $\eta = 10$ mPas the corrected viscosity is 3.4% lower and $\eta_{\text{corr.}}$ becomes 9.66 mPas. At $\eta = 1.5$ mPas, $\eta_{\text{corr.}} = 1.46$ mPas or 2.5% lower than the experimentally observed viscosity.

For viscosities in the range observed for NaCl-AlCl₃ mixtures, Equation (2) yields a correction factor about 0.5%

[3] W. Brockner, K. Tørklep and H.A. Øye: "Viscosity of Aluminium Chloride and Acidic Sodium Chloroaluminate Melts", Ber. Bunsenges. Phys. Chem. 83 (1979) 1.

below the 96.8% correction given in ref. [3]. This is due to a general 25 mm increase in liquid heights from the NaCl-AlCl₃ investigation. The reason for not including the meniscus correction in the tabulated viscosities has been stated in ref. [3]: the correction is empirical, and future theoretical (or experimental) work may lead to improved corrections for surface effects.

Arrhenius temperature plots are given in Figure 1, which also contains results obtained in the binary LiCl-AlCl₃ system [1]. The composition dependency of the viscosity at 200°C (the lowest common experimental temperature) is indicated in Figure 2, where the curves for logarithmic viscosities connect points at equal AlCl₃ contents*). The system is hence considered as a quasi-binary mixture of the binaries NaCl-AlCl₃ and LiCl-AlCl₃. There are negative deviations from the Arrhenius mixture rule except at 70 mol% AlCl₃ (the deviation at 60 mol% is also very small), an observation that may possibly be given a structural interpretation.

*) The NaCl/AlCl₃ spherecup results in Figure 2 have been multiplied with a correction factor 0.99, which comprises a -0.5% correction [3] to the spherecup equations and a -0.5% correction for the 25 mm height difference (see above).

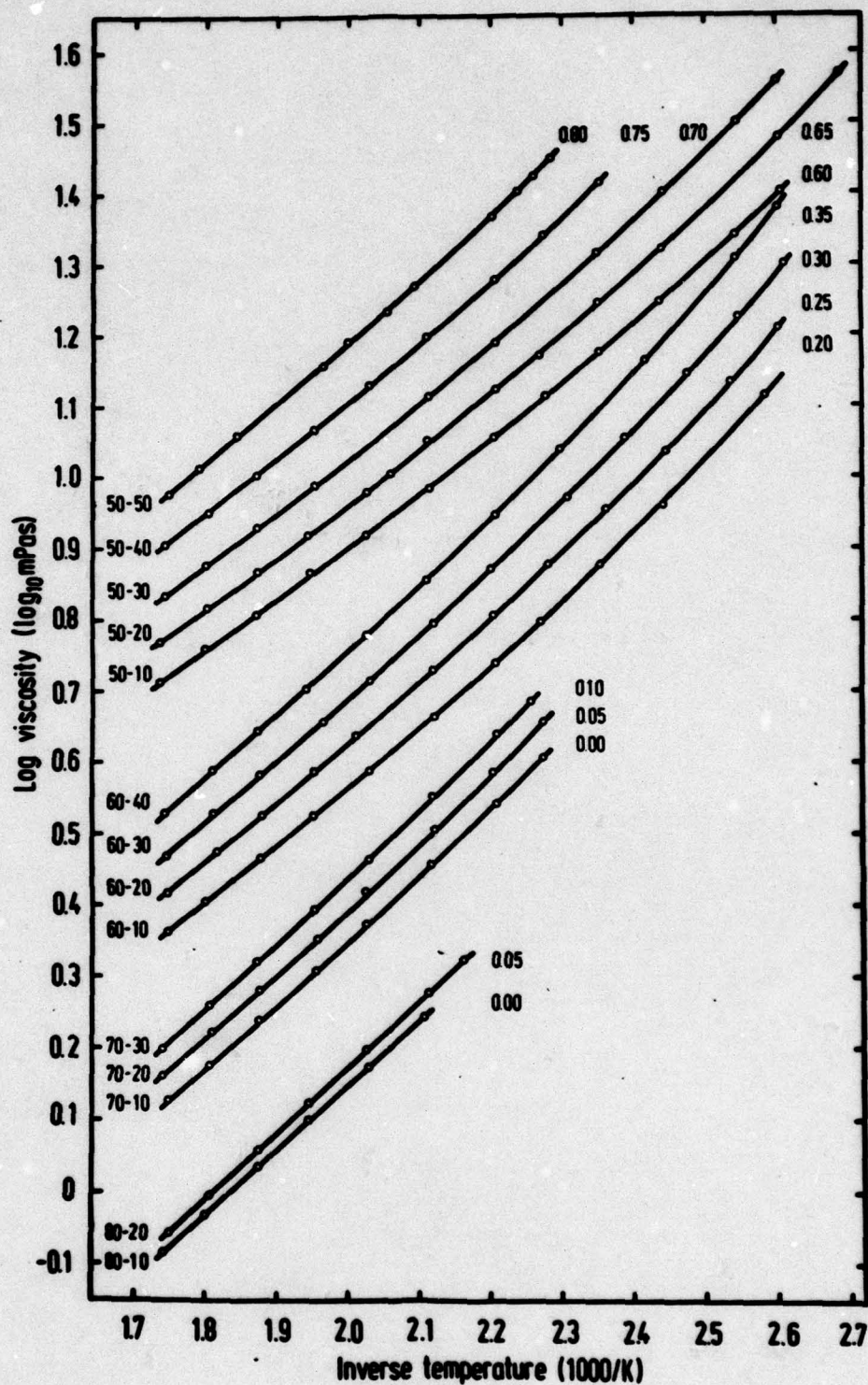


Figure 1. Viscosity of ternary mixtures of AlCl_3 - LiCl - NaCl . Melt compositions in mol% AlCl_3 - LiCl are given to the left. The curves have been displaced upwards (spaced) with the values at the right, which should be subtracted from the ordinate values to give correct logarithmic viscosities.

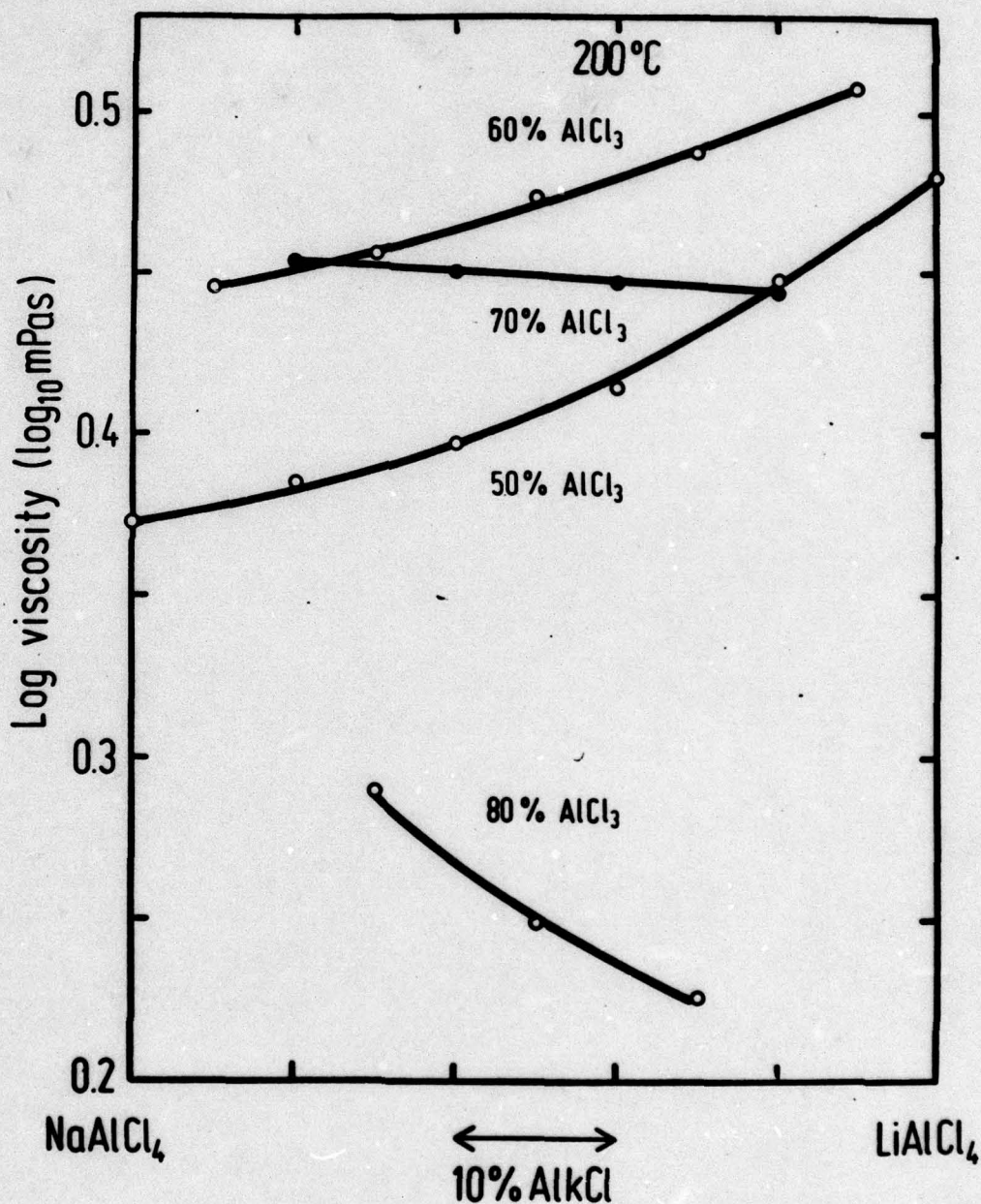


Figure 2. Viscosity of ternary AlCl_3 - LiCl - NaCl mixtures as function of composition (mol%) at 200°C.

~ **Table 2.** Parameters in Equation (1) for the viscosity of ternary LiCl-NaCl-AlCl₃ melts, with standard deviations (SD). The relative SD (%) of η in the fit is also given.

Al-Li-Na, mol%	Temp. span, K	Exp. points	A	SD·10 ³	B	SD	C	SD·10 ³	TM, K	SD, %
50-40-10	424-573	36	2.340	1.1	1764	4.5	0.4210	9.2	495.40	0.19
50-30-20	384-574	52	2.583	1.1	1712	3.3	0.3204	3.1	473.65	0.28
50-20-30	371-576	52	2.650	1.8	1671	4.7	0.2886	3.6	465.70	0.37
50-10-40	383-576	50	2.503	1.7	1634	5.2	0.2489	4.8	469.10	0.39
60-30-10	382-574	45	3.148	1.3	1927	3.1	0.3535	2.8	470.42	0.25
60-20-20	383-573	50	3.020	1.1	1881	2.9	0.3250	2.8	471.35	0.19
60-10-30	386-572	44	2.758	2.0	1788	5.7	0.3823	5.5	477.20	0.25
70-20-10	439-574	32	2.133	1.4	2041	7.3	0.3212	1.9	503.40	0.23
70-10-20	439-572	32	2.164	1.4	2013	7.2	0.2572	1.9	503.45	0.25
80-10-10	474-574	24	1.159	0.4	4121	4.4	0	-	524.15	0.14

**Table 1a. Viscosity of LiCl-NaCl-AlCl₃ melts.
50 mol% AlCl₃. Mean values.**

Composition, mol% LiCl	Temperature, °C	Mean viscosity, mPas	SD, %
40	300.8	1.429	0.08
	281.3	1.587	0.04
	261.3	1.787	0.01
	239.0	2.069	0.05
	219.3	2.395	0.05
	200.4	2.798	0.08
	180.0	3.368	0.01
	166.6	3.888	0.09
	151.6	4.622	0.07
	136.8	5.950	0.03
	121.4	7.536	0.03
30	260.9	1.694	0.04
	282.0	1.500	0.05
	300.8	1.358	0.02
	238.5	1.941	0.04
	217.8	2.254	0.04
	239.8	1.923	0.08
	200.1	2.585	0.05
	179.9	3.086	0.02
	166.9	3.517	0.01
	152.3	4.123	0.02
	136.3	5.010	0.03
	119.6	6.318	0.03
20	111.5	7.188	0.01
	260.6	1.645	0.04
	281.8	1.464	0.02
	303.1	1.314	0.08
	241.3	1.851	0.04
	220.1	2.134	0.10
	212.4	2.256	0.01
	179.9	2.969	0.04
	167.6	3.311	0.08
	152.0	3.933	0.04
	136.5	4.677	0.02
	120.0	5.851	0.01
10	110.8	6.731	0.03
	98.7	8.227	0.01
	282.7	1.441	0.06
	302.9	1.294	0.10
	260.7	1.607	0.04
	240.1	1.838	0.04
	220.4	2.083	0.09
	200.0	2.413	0.06
	180.4	2.852	0.01
	165.7	3.253	0.17
	151.9	3.761	0.03
	136.8	4.429	0.03
	120.0	5.503	0.02
	110.2	6.328	0.06

**Table 1b. Viscosity of LiCl-NaCl-AlCl₃ melts.
60 mol% AlCl₃. Mean values.**

Composition, mol% LiCl	Temperature, °C	Mean viscosity, mPas	SD, %
30	278.9	1.686	0.06
	301.3	1.473	0.08
	235.4	2.263	0.03
	198.3	3.116	0.07
	259.9	1.909	0.02
	219.2	2.593	0.01
	180.9	3.710	0.02
	160.0	4.686	0.02
	145.3	5.660	0.01
	130.4	7.006	0.08
	119.3	8.388	0.04
	109.5	9.994	0.01
20	258.7	1.890	0.07
	277.3	1.672	0.05
	299.4	1.470	0.05
	198.5	3.005	0.01
	223.8	2.427	0.02
	238.6	2.167	0.04
	180.3	3.589	0.03
	165.1	4.222	0.03
	150.0	5.066	0.07
	135.2	6.163	0.02
	120.9	7.640	0.04
	110.7	9.094	0.01
10	299.0	1.453	0.01
	238.9	2.108	0.06
	282.3	1.596	0.06
	259.3	1.834	0.03
	179.8	3.450	0.02
	198.1	2.903	0.02
	219.4	2.438	0.04
	167.0	3.943	0.02
	151.0	4.754	0.08
	136.0	5.746	0.03
	113.5	8.224	0.05

Table 1c. Viscosity of LiCl-NaCl-AlCl₃ melts.
70 mol% AlCl₃. Mean values.

Composition, mol% LiCl	Temperature, °C	Mean viscosity, mPas	SD, %
20	259.6	1.699	0.05
	301.2	1.289	0.07
	279.2	1.481	0.03
	237.7	2.002	0.03
	219.6	2.342	0.04
	198.1	2.841	0.05
	180.2	3.439	0.05
	166.3	4.020	0.02
10	280.2	1.501	0.06
	299.1	1.335	0.03
	199.0	2.846	0.01
	220.5	2.359	0.06
	238.4	2.024	0.02
	259.8	1.726	0.05
	179.3	3.470	0.05
	166.1	4.026	0.05

Table 1d. Viscosity of LiCl-NaCl-AlCl₃ melts.
80 mol% AlCl₃. Mean values.

Composition, mol% LiCl	Temperature, °C	Mean viscosity, mPas	SD, %
10	260.3	1.084	0.03
	282.4	0.927	0.08
	301.0	0.822	0.11
	240.6	1.255	0.06
	220.0	1.485	0.01
	201.6	1.751	0.04

APPENDIX

The following Tables A1-A10 contain the entire experimental material from the viscosity investigations of ternary AlCl_3 - LiCl - NaCl melts, arranged in order of increasing AlCl_3 and LiCl contents. The chronological order of measurement is given below.

AlCl_3 - LiCl - NaCl , mol%	Table no.
60-30-10	A7
60-20-20	A6
60-10-30	A5
70-20-10	A9
70-10-20	A8
50-30-20	A3
80-10-10	A10
50-20-30	A2
50-10-40	A1
50-40-10	A4

Within each table, results are listed in the order measured.

Table A1. Viscosity of 50 mol% AlCl_3 - 10 mol% LiCl - 40 mol% NaCl .

Temperature, $^{\circ}\text{C}$	Viscosity, mPas	$\text{SD} \cdot 10^3$, mPas
282.7	1.443	1
	1.441	1
	1.441	1
	1.440	1
302.9	1.290	2
	1.295	1
	1.296	1
	1.295	1
260.7	1.609	2
	1.607	1
	1.608	1
	1.606	1
240.1	1.837	3
	1.840	2
	1.839	1
	1.837	1
220.4	2.080	2
	2.086	1
	2.086	1
	2.079	1
200.0	2.418	2
	2.414	1
	2.411	1
	2.410	1
	2.411	2
180.4	2.852	1
	2.852	1
	2.852	2
	2.852	1
165.7	3.264	2
	3.260	2
	3.245	2
	3.242	2
151.9	3.763	2
	3.761	2
	3.762	2
	3.758	3
136.8	4.432	3
	4.426	3
	4.430	3
	4.430	3
120.0	5.501	3
	5.506	3
	5.505	4
	5.502	4
110.2	6.324	4
	6.321	5
	6.317	5
	6.307	4

Table A2. Viscosity of 50 mol% AlCl_3 - 20 mol% LiCl -
30 mol% NaCl

Temperature, $^{\circ}\text{C}$	Viscosity, mPas	$\text{SD} \cdot 10^3$, mPas
260.6	1.647	1
	1.644	1
	1.644	1
	1.643	1
281.8	1.465	1
	1.464	1
	1.464	1
	1.463	1
303.1	1.312	1
	1.315	1
	1.316	2
	1.312	2
241.3	1.852	1
	1.850	1
	1.850	1
	1.851	1
220.1	2.140	2
	2.133	1
	2.131	1
	2.132	1
212.4	2.256	1
	2.255	2
	2.256	1
	2.257	2
179.9	2.972	2
	2.970	2
	2.968	2
	2.967	2
167.6	3.303	3
	3.314	2
	3.314	2
	3.313	2
152.0	3.937	4
	3.932	1
	3.931	2
	3.930	2
136.5	4.679	2
	4.678	2
	4.675	2
	4.675	2
120.0	5.852	3
	5.854	4
	5.851	3

To be continued

(Table A2 , cont'd)

Temperature, °C	Viscosity, mPas	SD·10 ³ mPas
110.8	6.728	3
	6.730	5
	6.735	3
	6.733	5
98.7	8.229	5
	8.228	5
	8.224	5
	8.225	4

Table A3. Viscosity of 50 mol% AlCl_3 - 30 mol% LiCl -
20 mol% NaCl .

Temperature, $^{\circ}\text{C}$	Viscosity, mPas	$\text{SD} \cdot 10^3$, mPas
260.9	1.693	1
	1.694	1
	1.695	1
	1.694	2
282.0	1.502	1
	1.500	1
	1.499	1
	1.499	1
300.8	1.359	1
	1.358	1
	1.358	1
	1.358	1
238.5	1.941	1
	1.940	1
	1.940	2
	1.944	1
217.8	2.255	2
	2.255	2
	2.253	2
	2.251	2
239.8	1.930	2
	1.924	1
	1.928	2
	1.925	1
200.1	2.582	3
	2.588	1
	2.585	2
	2.585	2
179.9	3.088	2
	3.086	2
	3.086	2
	3.084	2
166.9	3.518	3
	3.516	3
	3.517	3
	3.518	3
152.3	4.122	3
	4.124	3
	4.125	3
	4.121	3
136.3	5.012	3
	5.006	5
	5.010	4
	5.011	4

To be continued

(Table A3 cont'd)

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
119.6	6.316	3
	6.320	4
	6.314	5
	6.321	5
111.5	7.186	6
	7.189	4
	7.188	6
	7.189	5

**Table A4. Viscosity of 50 mol% AlCl₃ - 40 mol% LiCl -
10 mol% NaCl.**

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
300.8	1.432	2
	1.430	2
	1.426	1
	1.428	1
281.3	1.586	1
	1.587	1
	1.588	1
	1.586	1
261.3	1.787	1
	1.787	1
	1.786	1
	1.787	2
239.0	2.071	1
	2.069	1
	2.070	2
	2.066	2
219.3	2.392	2
	2.397	2
	2.397	1
	2.395	2
200.4	2.803	2
	2.798	1
	2.797	3
	2.793	
180.0	3.368	2
	3.370	3
	3.368	2
	3.369	3
166.6	3.894	2
	3.882	2
	3.881	2
	3.878	2
151.6	4.630	4
	4.622	3
	4.619	3
	4.616	3
136.8	5.954	3
	5.947	3
	5.952	3
	5.947	4
121.4	7.541	3
	7.539	4
	7.534	4
	7.531	5

Table A5. Viscosity of 60 mol% AlCl_3 - 10 mol% LiCl - 30 mol% NaCl .

Temperature, $^{\circ}\text{C}$	Viscosity, mPas	$\text{SD} \cdot 10^3$, mPas
299.0	1.453	2
	1.453	1
	1.454	2
	1.453	1
238.9	2.112	3
	2.108	2
	2.106	2
	2.106	2
282.3	1.595	2
	1.596	3
	1.599	2
	1.595	4
259.3	1.836	2
	1.834	3
	1.834	5
	1.834	2
179.8	3.449	2
	3.450	2
	3.451	2
	3.450	2
198.1	2.904	2
	2.902	2
	2.905	3
	2.903	3
219.4	2.441	1
	2.438	1
	2.439	2
	2.437	2
167.0	3.944	2
	3.943	3
	3.942	3
	3.944	4
151.0	4.762	4
	4.755	3
	4.745	4
	4.753	4
136.0	5.747	5
	5.745	5
	5.742	4
	5.751	5
113.5	8.221	12
	8.217	8
	8.221	10
	8.235	6

Table A6. Viscosity of 60 mol% AlCl_3 - 20 mol% LiCl -
20 mol% NaCl_3 .

Temperature, °C	Viscosity, mPas	$\text{SD} \cdot 10^3$ mPas
258.7	1.894	2
	1.888	1
	1.888	1
	1.889	1
277.3	1.672	1
	1.673	1
	1.674	1
	1.669	2
	1.671	2
299.4	1.472	1
	1.470	3
	1.470	2
	1.468	2
198.5	3.005	2
	3.005	2
	3.004	2
	3.004	3
223.8	2.426	2
	2.428	2
	2.426	3
	2.427	2
238.6	2.169	1
	2.167	1
	2.168	2
	2.164	2
180.3	3.591	2
	3.587	3
	3.587	3
	3.590	4
165.1	4.221	5
	4.225	3
	4.220	2
	4.221	2
150.0	5.073	5
	5.068	3
	5.066	4
	5.057	3
135.3	6.165	4
	6.165	5
	6.162	5
	6.159	5

To be continued

(Table A6, cont'd)

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
120.9	7.643	6
	7.635	5
	7.636	5
	7.647	7
110.7	9.097	9
	9.092	6
	9.084	7
	9.097	8

Table A7. Viscosity of 60 mol% AlCl₃ - 30 mol% LiCl - 10 mol% NaCl.

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
278.9	1.689	2
	1.687	1
	1.685	1
	1.685	1
301.3	1.477	2
	1.474	1
	1.473	1
	1.472	1
	1.470	1
235.4	2.262	3
	2.264	2
	2.265	2
	2.262	2
198.3	3.123	3
	3.113	3
	3.114	2
	3.116	2
259.9	1.910	1
	1.908	1
	1.909	1
	1.909	2
219.2	2.593	3
	2.593	2
	2.594	1
	2.593	2
180.9	3.710	2
	3.710	2
	3.712	3
	3.709	3
160.0	4.709	4
	4.685	3
	4.687	3
	4.684	4
145.3	5.659	4
	5.661	4
	5.660	3
130.4	6.990	6
	7.013	4
	7.010	5
	7.012	4

To be continued

(Table A7, cont'd)

Temperature, °C	Viscosity, mPas	SD·10 ³ , mPas
119.3	8.375	6
	8.391	5
	8.397	5
	8.388	6
	8.387	5
109.5	9.996	7
	9.995	6
	9.994	7
	9.993	7

Table A8. Viscosity of 70 mol% AlCl_3 - 10 mol% LiCl - 20 mol% NaCl .

Temperature, $^{\circ}\text{C}$	Viscosity, mPas	$\text{SD} \cdot 10^3$, mPas
280.2	1.502	2
	1.498	2
	1.500	1
	1.502	1
299.1	1.335	3
	1.334	2
	1.336	1
	1.336	1
199.0	2.845	2
	2.847	2
	2.847	3
	2.846	3
220.5	2.362	2
	2.357	2
	2.361	1
	2.357	1
238.4	2.024	1
	2.024	3
	2.024	2
	2.025	2
258.9	1.726	3
	1.724	2
	1.727	2
	1.726	2
179.3	3.465	3
	3.474	2
	3.472	3
	3.470	3
166.1	4.032	3
	4.024	3
	4.026	3
	4.024	3

Table A9. Viscosity of 70 mol% AlCl_3 - 20 mol% LiCl - 10 mol% NaCl

Temperature, $^{\circ}\text{C}$	Viscosity, mPas	$\text{SD} \cdot 10^3$, mPas
259.6	1.699	2
	1.700	2
	1.701	3
	1.697	6
301.2	1.286	1
	1.288	1
	1.290	1
	1.290	2
279.2	1.480	3
	1.482	2
	1.482	2
	1.481	5
237.7	2.001	2
	2.002	2
	2.004	2
	2.003	3
219.6	2.340	5
	2.344	2
	2.342	2
	2.342	3
198.1	2.844	2
	2.840	2
	2.843	2
	2.837	3
180.2	3.436	1
	3.439	2
	3.443	2
	3.438	2
166.3	4.022	3
	4.020	2
	4.019	4
	4.019	3

Table A10. Viscosity of 80 mol% AlCl_3 - 10 mol% LiCl -
10 mol% NaCl .

Temperature, $^{\circ}\text{C}$	Viscosity, mPas	$\text{SD} \cdot 10^3$, mPas
260.3	1.083	1
	1.083	1
	1.084	1
	1.085	1
282.4	0.929	1
	0.927	1
	0.925	2
	0.927	1
301.0	0.824	1
	0.821	1
	0.821	1
	0.821	2
240.6	1.257	2
	1.254	1
	1.255	1
	1.254	1
220.0	1.485	1
	1.485	1
	1.485	1
	1.486	1
201.6	1.750	1
	1.752	1
	1.752	1
	1.749	1

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A precision oscillation viscometer for determination of the viscosity for low-viscous salts with high vapour pressures has been developed. The viscosity is determined from the damping of a hollow cylinder filled with the salt to be investigated. The viscosity of following systems has been determined: $AlCl_3$, The binary					

ABSTRACT: systems LiCl-AlCl_3 and NaCl-AlCl_3 . The ternary systems LiCl-NaCl-AlCl_3 with $0.50 \leq X_{\text{AlCl}_3} \leq 0.80$ and $100^\circ\text{C} < t < 300^\circ\text{C}$. Melt modelling has allowed a rational description of the viscosity variation as function of composition and temperature within 0.4%.